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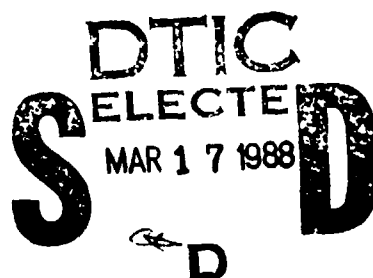
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# SUMMARY REPORT OF THE SUMMER CONFERENCE

## DARPA-MATERIALS RESEARCH COUNCIL

La Jolla, California



July 1987

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SUMMARY REPORT OF THE SUMMER CONFERENCE

of the

DARPA-MATERIALS RESEARCH COUNCIL

La Jolla, California

July 1987

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## INTRODUCTION

This report is a summary of the 1987 DARPA-Materials Research Council Summer Conference which was held in La Jolla, California, during the period from July 6, 1987 through July 30, 1987. It is a report which is being submitted to DARPA early in the contract period to enable them to utilize the results of the various workshops in a timely fashion. A later report will be issued to include the materials generated at workshops held at periods other than those of the Summer Conference.

The principal task of the ONR-DARPA Grant is to bring together a group of the Country's leading materials scientists and engineers for an extended period, usually the month of July, to permit them to apply their combined talents to the planning and scoping of future materials research areas for the Department of Defense.

During the year workshops, and in some cases program reviews, are attended by smaller groups of Council members and their reports are made directly to DARPA. This is a growing activity of the Council and these reports in the future will be included in the report submitted at the end of the contract year.

The technical direction of the Council is by a Steering Committee made up of five representative members of the Council who work with DARPA management. The Committee for 1987 is given in the following table. The Steering Committee selects the relevant topics for the annual Summer Conference and works with the other council members in developing new areas in materials research. The membership on the Steering Committee and of the Council varies from year to year depending on the research areas that are of major interest to the Department of Defense. The Council membership for 1987 is given in the following table.

The Council also serves as a resource for the DARPA Defense Sciences Divisions and other DARPA offices. The DARPA participants in the 1987 Summer Conference are given in the following listing.

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J. D. Murphy  
J. A. Neff  
I. D. Skurnick  
F. W. Patten  
P. A. Parrish  
A. Prabhakar  
K. Rhyne  
H. Wisniewski  
G. Farnum

The agenda for a Summer Conference is prepared initially during the prior year's conference with input from DARPA and the Council. This is refined at subsequent Steering Committee meetings and the workshops are organized. The calendar for the 1987 Summer Conference is shown in the attached figure.

# JULY 1987 SUMMER CONFERENCE

(Conference Dates are July 7 through 31)

S	MONDAY	TUESDAY	WEDNESDAY	THURSDAY	FRIDAY	S
6	COMPOSITE CANNON?	7 DARPAMRC PRESENTATIONS	8 /	9 DIAMOND LIKE MATERIALS	10 Steering Committee Meeting	
13	HIGH SPEED CIRCUITS COMPOSITES	14	15 (Tank AM) /	16 (Tank AM) INSTRUMENTATION	17	
20	NUMERICAL SIMULATION & MATHEMATICAL METHODS	21	22 SUPERCONDUCTING MATERIALS	23 NONLINEAR OPTICS	24 CAL MATERIALS Steering Committee Meeting	
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In structuring the agenda, time is made available to permit the addition of additional workshops that arise during the periods while the regular workshops are being organized. The first workshop, scheduled for July 6, 1987, was one of these. It was generated by a NMAB report on "Non-Conventional Materials for Gun Tubes", NMAB Report NO. 423, and a DARPA-Army meeting held in Washington on December 10, 1986, to explore the feasibility and Army interest in using advanced materials to improve the performance of gun systems. As a result of this meeting a one-day workshop was scheduled for the Materials Summer Conference to examine in some detail what steps could be taken to implement such a program in the Materials Science Division of DARPA. The agenda of that meeting and the attendance list follows. As a result of that workshop, a paper was generated and some comments were offered; they appear after the agenda and attendance list.

## AGENDA

### ADVANCED MATERIALS GUN SYSTEM

July 6, 1987

Opening Remarks and Program Goals  
A. G. Evans (MRC), Gene Farnum (DARPA)

A Good Gun from the User Perspective  
Ray Goldstein (ARDEC)

Findings and Issues from the NMAB Study "Applications of Non-Conventional  
Materials to Guns and Gun Tubes"  
Frank Gerstle (Sandia National Lab.)

Interior Ballistics -- Physics, Chemistry and Trade-Offs  
Stanley Goddard (Battelle)

Discussion

## ATTENDEES

A. G. Evans	MRC
G. Farnum	DARPA
S. Goddard	BATTELLE
F. Gerstle	SANDIA
B. Budiansky	MRC
J. Hutchinson	MRC
H. Ehrenreich	MRC
M. Wrighton	MRC
R. Mehrabian	MRC
J. Margrave	MRC
M. Dresselhaus	MRC
R. McMeeking	MRC
N. R. Katz	AMTL
J. Williams	MRC
B. Wilcox	DARPA
R. Reynolds	DARPA
J. Soble	MRC
K. Rhyne	DARPA
M. Sinnott	MRC
G. Whitesides	MRC

## ADVANCED MATERIAL GUN BARRELS

R. Mehrabian, A. G. Evans, B. Budiansky, J. W. Hutchinson

### SUMMARY

The purpose of this workshop was to examine the application of advanced materials to guns and gun barrels. Focus was primarily placed on increasing barrel lifetimes while increasing muzzle velocity and rate-of-fire. The available knowledge-base on gun barrel erosion and failure was reviewed and the utility of composite barrels examined. Specific emphasis was placed on thermal and stress modeling to calculate temperature profiles and stress distributions. Computer programs were developed by the MRC members and collaborators for this purpose. Calculations were carried out for composite barrels with different ceramic liners and 4340 low alloy steel jackets. It was found that erosion and cracking problems could be greatly alleviated by a judicious selection of materials combinations and barrel construction, with the ceramic liner initially shrunk fit, as elaborated below. A 75mm diameter, high velocity cannon with a wall thickness of 25mm was used in the calculations. Ceramic insert thicknesses of up to 5mm were chosen.

The preliminary conclusions, based on the analysis conducted by the MRC, concern conditions and materials that inhibit bore erosion and liner cracking. The jacket system has yet to be systematically investigated. The implications appear to be intuitively reasonable and are as follows: (Key points) —————

- A graded system is necessary, consisting of a ceramic/ceramic-matrix composite/metal-matrix composite/alloy. The first layer is chemically stable and has a high melting temperature to inhibit bore erosion. The second layer is both elastic and has high toughness and would inhibit cracking/distortion from the mechanical and thermal stresses. The third (MMC) layer has the strength and toughness needed to

confine the expansion of the liner. Water cooling may be needed to for this purpose.

- To limit tensile stress on the liner from the thermal gradient, the jacket thermal expansion coefficient should be similar to that of the ceramic.
- To limit tensile stress in the liner from the internal pressure, the jacket should have a modulus comparable to that of the liner.
- To minimize the heat flow into the barrel, the heat diffusivity of the ceramic should be high.
- Shrink fitting of the liner will be necessary, using a thin compliant layer.
- The liner should extend out to the muzzle to inhibit thermal cycle cracking.
- Water cooling of the jacket should be used when possible to resist liner cracking and jacket distortion.

## INTRODUCTION

The gun barrel is basically a tubular pressure vessel with opening at the muzzle end. Rapid pressure rise is produced by detonation of the propellant and the projectile is accelerated down the barrel. At a location near the breech, pressure reaches a maximum and then, gradually declines. The muzzle velocity and the size of the projectile determine the pressure history in the tube.

Each firing produces a heat pulse and a corresponding temperature rise which quickly reaches a peak at the bore surface. Subsequent heat conduction into the body of the bore reduces the surface temperature to a substantially lower value-often referred to as the residual bore surface temperature. The average barrel temperature increases with increasing number of firings, unless the jacket is water cooled, whereupon a steady state heat flow condition can be reached after a number of firings. Thermal profiles in the barrel are a function of gun caliber, projectile velocity, firing rate and schedule. In general, the total heat input to the gun barrel decreases with decreasing caliber.

Gun barrel failure modes vary with caliber. In small arm systems, the temperatures are moderate and mechanical damage is caused by propellant pressure on the weakened barrel surface. Many rounds need to be fired before sufficiently high temperatures are reached for bore erosion to occur. On the other hand, in very large gun barrels very high peak bore surface temperatures are quickly reached and melting erosion can occur.

Bore erosion is generally ascribed to several factors. These include:

- Chemical reaction with the propellant gas followed by removal of the reaction products.
- High velocity "scrubbing" by the gas and solid particles, including abrasion and wear by the projectile.
- High temperatures generated by firing and convective propellant gas flow along the bore surface result in "heat checking" at low temperatures and a thin molten layer at high temperatures. The latter is ejected by the propellant gases.

Available solutions to bore erosion problems include:

- Propellant Modifications
  - lower flame temperatures
  - ablative additive - e.g. to coat the bore and reduce convective heat transfer
- Barrel Modifications
  - improved barrel materials including chromium and stellite liners
  - external cooling

Development of high impetus propellants, for higher muzzle velocities, is essentially limited by the properties of the gun steel melting temperature, its high temperature mechanical properties, and reactivity with the propellant gases. Thus, even though 4340 low alloy steel, sometimes with a liner (chromium), is the material of choice

for guns with conventional ballistics (especially in combination with ablative additives), new high temperature, high strength composites are needed for advanced high muzzle velocity systems.

The behavior of a composite barrel consisting of a ceramic or a ceramic composite liner with a metal or metal matrix composite jacket involves coupled thermal and mechanical considerations, based on established principles. The choice of materials and designs are readily explored using simple analytical and experimental simulation of the salient processes, as well as numerical analysis. Experience with gun barrel operation, as well as studies of thermal gradients and stresses, provide the framework of understanding needed to systematically address the problem. As noted above, very high transient temperatures develop near the bore during each shot, with a steep radial gradient. The average temperature increases with each shot leading to a corresponding, gradual increase in the peak temperature. A corresponding pressure pulse forms behind the projectile, within the bore (Fig. 1). This pressure is essentially uniform at any instant, but decreases systematically as the projectile propagates along the barrel.

The stresses and temperatures experienced within the barrel provide three possible failure modes: erosion by bore melting, cracking of the liner, and plastic deformation of the jacket. Each of these effects requires consideration, separately and in combination, in order to create an optimal design. The avoidance of significant erosion principally requires that the bore temperature be maintained below the melting temperature of the liner. The observed incidence of circumferential cracking of ceramic liners, near the end, indicates that net axial tensile stress must be developed during the firing cycle. Tensile stresses caused by the pressure within the bore and by thermal cycling are candidate causes of the cracking problem. Finally, plastic deformation of the

metal matrix composite jacket is a potential problem. Such deformation would tend to expand the barrel and cause cracking of the liner upon thermal cycling.

## MATERIALS OF INTEREST

In this preliminary investigation, ceramic liners of principal interest would be materials capable of being fabricated in near net shape, such as by the Lanxide<sup>TM</sup> process. As noted later, the heat diffusivity is of particular importance, as well as the melting temperature and thermal expansion coefficient and, to a lesser extent, the elastic modulus. An important range of such variables is encompassed by selecting  $\text{Al}_2\text{O}_3$ ,  $\text{AlN}$  and  $\text{SiC}$  as the liner materials (Table 1). For the initial calculations, the jacket material has been a 4340 steel. However, various metal matrix composite systems having a range of elastic, thermal and mechanical properties would be examined in a continuation study.

Table I  
Properties of Liner Materials

Material	Elastic Modulus GPa	Exp. Coefficient $\alpha(\text{C}^{-1})$	Thermal Diffusion $K/C_p\rho$
$\text{Al}_2\text{O}_3$	400	$8 \times 10^{-6}$	0.22
$\text{AlN}$	320	$6 \times 10^{-6}$	
$\text{SiC}$	420	$4 \times 10^{-6}$	0.48

## THERMAL MODELS

A heat transfer model was developed based on earlier data reported by F.A. Vassallo<sup>1,2</sup>. Representative data for heat transfer coefficient and propellant gas temperature as a function of time are shown in Figures 2 and 3. These data were used to generate temperature profiles in a cannon with a wall thickness of 25mm firing at 120 rounds per minute. Initial calculations were carried out for a 4340 low alloy steel material to generate thermal profiles such as those reported by Vassallo<sup>1</sup> and the recent NMAB Report - 423 (1986). These data were then used as a baseline for further calculations of temperature distributions in various composite gun barrels. A thin ceramic insert in a 4340 low alloy steel jacket was used in all other calculations.

### (i) Heat Transfer Analysis

A detailed description of the heat transfer model is not given here since it is relatively straightforward. The heat balance equation for the interior nodes comprised of two different materials located at  $1 < i < n$  and  $n < i < m$  is simply the finite difference formulation of:

$$\partial T / \partial t = [\kappa / r] \left[ \partial / \partial r \right] (r \left[ \partial T / \partial r \right]) \quad (1)$$

where  $T$  is temperature,  $r$  is radius,  $t$  is time, and  $\kappa$  is thermal diffusivity. The boundary condition at the bore surface is,

$$\rho C_p V dT/dt = Q_{in} - Q_{out} \quad (2)$$

where:

$$Q_{in} = -h_G (T_I - T_G) (2\pi La) \quad 3(a)$$

$$Q_{out} = -k_i \partial T / \partial r [2\pi (a + \Delta r/2)L] \quad 3(b)$$

V is volume,  $\rho$  is density,  $T_G$  is propellant gas temperature, L is barrel length,  $h_G$  is heat transfer coefficient at propellant gas/bore interface and Q is heat flux. The boundary condition at the interface between the ceramic insert and the metal jacket is:

$$-k_n(-\partial T/\partial r [2\pi (r_n - \{\Delta r/2\})L]) + k_n(+\partial T/\partial r [2\pi (r_n + \{\Delta r/2\})L] = \rho C_p V \partial T/\partial t \quad (4)$$

The outer node, steel jacket surface, is subject to boundary condition similar to (2) and (3). However, for a water cooled jacket the temperature at  $r = b$  is fixed.

Bore surface temperatures as a function of time for an all steel barrel after rounds 1, 10 and 100 (Fig. 4) reveal that during the first round, the peak surface temperature significantly exceeds the austenitizing temperature (1088K) and during the 100th round exceeds the melting temperature (~1740K). Figure 5 shows a composite plot of peak bore surface temperature and bore surface residual temperature, as a function of number of rounds. These data closely correlate with those reported by Vassalo<sup>1</sup> and lend credence to the explanation that bore erosion in this type of cannon can be directly correlated with metallurgical transformations near the bore surface. Other observations have also shown (NMAB-423) that, below a certain threshold projectile kinetic energy, little or no heat checking or bore erosion takes place.

Heat checking, or surface cracking, is a form of thermal fatigue at the bore surface similar to the alligator skin appearance observed in other processes, such as die casting of copper in steel dies. When the bore surface temperature exceeds the austenitic transformation temperature of the steel, the martensite to austenite transformation results in a volume change. This volume change, partly assisted by the thermal compressive stresses, causes local yielding at the bore surface. This localized deformation is then followed, upon cooling, by tensile stresses that exceed the fracture strength of the

untempered martensite that forms from the austenite. More rapid bore erosion initiates when the bore surface temperature exceeds the melting temperature of the steel. The molten surface layer is then literally washed away or "scrubbed-out" by the moving projectile/propellant combination. Chemical interactions of the steel with the propellant gas could also aggravate bore erosion: for example, absorbed carbon and oxygen would lower the steel melting temperature. Furthermore, it is emphasized that a 250K increase in propellant temperature (Fig. 5) causes the peak surface temperature to reach the melting temperature of steel much earlier (at ~20 rounds).

Calculated temperature profiles for a composite cannon with 5mm thick  $\text{Al}_2\text{O}_3$  or SiC liners are shown in Figures 6 and 7. Note that both the peak and residual surface temperatures are significantly higher than for the all-steel barrel. However, even after 100 rounds these peak surface temperatures are much lower than the associated melting temperatures, because of the more refractory nature of the liner materials.

A sequence of computer calculations has been used to differentiate the effect of thermophysical properties of the bore material on bore surface peak temperatures. These results (Fig. 8) reveal that increasing the product,  $k/\rho C_p$ , (which is a measure the ability of the material to transmit heat from the surface into the interior) causes a significant reduction in peak bore surface temperatures. These predictions are in accordance with the results for  $\text{Al}_2\text{O}_3$  and SiC inserts, (where  $[k/\rho C_p]_{\text{SiC}} > [k/\rho C_p]_{\text{Al}_2\text{O}_3}$ ).

## STRESS ANALYSIS

A numerical program capable of evaluating stress distributions in the barrel has been developed (McMeeking) for a multilayer, orthotropic material system (i.e. the same circumferential and axial but different radial properties). A brief summary of the analysis is given in Appendix I. The stresses of interest are those exerted by the internal pressure

and those associated with thermal gradients. The initial calculations have been elastic, but plasticity would be introduced should the equivalent stress in the jacket exceed the flow stress. Elasticity allows the mechanical and thermal stresses to be linearly superimposed. Each contribution can thus be evaluated separately and later, combined with the appropriate temporal characteristics. Initial stresses generated by shrink fitting can also be superimposed (Appendix II).

### Radial and Circumferential Stresses

The radial and circumferential stresses created by the pressure have been evaluated for generalized plane strain, such that the full range of projectile conditions can be examined. The axial stresses are considered in the following section, because of important end effects not yet included in the numerical program. It is already evident from previous studies that the high modulus of the ceramic liner is a detrimental property in the presence of internal pressure, particularly when the liner is relatively thick. Consequently, for the present calculations, thin liners having a thickness about one tenth to one fifth the jacket thickness are used for analysis. The stresses have the non-dimensional form:

$$\sigma_{ij}/p = F_{ij}(t/a, b/a) \quad (5)$$

when  $p$  is the pressure,  $t$  is the liner thickness,  $a$  is the bore radius,  $b$  is the outer radius of the jacket and  $F_{ij}$  are the functions plotted in Fig. 9, for  $Al_2O_3$  within a steel jacket. Using a typical pressure  $P$  of order 400MPa, the circumferential tensile stresses are in the range, 1.2 GPa ( $b/a \approx 1.5$ ).

The radial and circumferential stresses generated by thermal gradients are determined from the thermal profiles derived in section 3, at the peak bore temperatures. Some of the results are plotted in Fig. 10. Of particular importance is the existence of

tensile stress in the ceramic liner near its outer diameter. These stresses diminish as the relative liner thickness decreases and are smaller for  $\text{Al}_2\text{O}_3$  than SiC. The trends at small thickness are consistent with an analytic approximation (Appendix III) revealing that the tensile stresses scale both with the difference in expansion between the liner and jacket and with the average jacket temperature. It appears, therefore, that thin liner having a close thermal expansion match with the jacket, as well as jacket cooling, are preferred conditions to avoid thermal fracture of the ceramic liner.

### Axial Stresses

Various sources of axial stress exist caused by thermal gradients and by the pressure pulse. Of particular concern for ceramic-lined barrels are axial tensile stresses near the bore. Such stresses can be generated by at least three phenomena: by thermal cycling, by inertial effects and by the pressure pulse.

Thermal cycling can generate axial residual tension near the end of the ceramic liner when either slip or yielding occur at the liner/jacket interface. Specifically, upon heating, axial expansion of the bore creates singular stresses that motivate slip at the end. The axial stresses in the ceramic liner (uniform across the liner radius) have the axial form depicted in Fig 11; zero at the end, rising linearly at a rate governed by the shear resistance of the interface. However, upon cooling, reverse slip must occur near the ends, such that at ambient temperatures, residual axial tension develops (Fig. 11). The peak residual tension has a magnitude governed by the shear resistance of the interface and the temperature amplitude of the thermal cycle. Such thermal cycling effects are regarded as a likely source of the circumferential cracks observed in ceramic lined guns. This premise could be verified by simply conducting thermal cycling tests, involving internal heating and cooling, and inspecting for cracks. However, even without such tests, it is apparent that the residual stress can be reduced by extending the liner as

far as possible from the breech, up to the muzzle, where the cyclic temperature amplitudes are small.

When the projectile velocity is sufficiently high that the stress wave transit time along the barrel is much less than the projectile transit time, inertia prohibits the barrel from contracting in response to the internal pressure near the breech. A condition of zero axial strain is then approached, leading to the development of radially uniform axial tension (for  $\text{Al}_2\text{O}_3/\text{steel}$ ,  $\sigma_{zz}/p = 0.5$ ). Finally, at the pressure front in the barrel, local distortions occur, leading to bulging. Analysis of this phenomenon indicates the existence of a small zone of axial tension in a boundary layer near the bore (Fig. 12). The amplitude and depth of the tensile stress scale with the bore radius.

## DISCUSSION

One of the obvious difficulties in using the preceding information about temperatures and stresses concerns the selection of 'failure' criteria that involve the appropriate superposition of the heat and pressure pulses. In order to provide a perspective for the further discussion of design principles, some of the known observations are first reviewed and interpreted. The incidence of axial splitting of brittle liners has never been reported. Yet, the largest tensile stress from the pressure pulse and bore heating occur circumferentially, suggesting that the compressive stresses from shrink fitting have in all cases been large enough to offset the tensile stress. This premise is also supported by the observation of circumferential cracks in the ceramic, located at the end remote from the breech. Specifically, the axial tensions from the pressure pulse have their largest value near the breech and not at the cracking site, near the end of the liner. The principal source of ceramic cracking is thus regarded as an end effect, exacerbated by thermal cycling. Consequently, liner cracking could seemingly be

alleviated as a problem by extending the liner out to the muzzle and by optimizing the shrink fit stresses, such that net axial tension can be avoided.

With the above information as background, it is possible to conduct a preliminary sensitivity study. When the ceramic liner is relatively thin ( $< 0.1 b$ , where  $b$  is the outer radius of the jacket), the sensitivity of the axial stresses to the elastic modulus is small, within the available range. However, the thermal expansion coefficient,  $\alpha$  is very important. Specifically,  $\alpha$  for the thin liner should be comparable to that of the jacket, such that the thermal gradient from firing does not eliminate the shrink fit compression in the liner. The requisite range of  $\alpha$  depends, of course, on the thermal properties of the barrel materials, the liner thickness and the projectile velocity. Further studies of trends with  $\alpha$  are recommended. Another critical parameter for the ceramic is the heat diffusivity,  $k/\rho C_p$ . Typically, a high diffusivity is needed to inhibit bore melting. However, it is also noted that the thermal diffusivity  $k/\rho C_p$ , should not be so large that the temperature rise in the jacket would allow the shear stresses in the jacket to cause plastic deformation or creep.

A judicious choice of material properties, coupled with initial shrink fitting and adequate extension of the ceramic liner to the muzzle, can maintain the inner portion of the liner in compression. It is not obvious, therefore, that high strength and toughness are required for the ceramic at the bore. Furthermore cracking of the liner is most likely to initiate at its outer surface. A graded liner would thus appear desirable with fiber reinforcement on the cooler outside, to limit cracking, and matrix only at the hot bore to avoid chemical reactions and eutectic formation between matrix and fiber.

The choice of jacket material has not yet been addressed. However, as conditions are optimized to avoid erosion and liner cracking, larger shear stress must be generated in the jacket and possibly, high temperatures, leading to a greater tendency for jacket distortion by deformation and creep. Thermal cycling problems in metal matrix

composite (MMC) jackets, such as ratchetting, must also be a concern. Water cooling of the jacket would substantially alleviate these problems. A continuation study should examine the stresses and temperatures in candidate MMC jacket materials.

## Appendix I

### Stress Analysis

The governing equations are;

$$d\sigma_{rr}/dr + \sigma_{rr} - (\sigma_{\theta\theta})/r = 0 \quad (A1)$$

At the interfaces,  $\sigma_r$  is continuous. Also,

$$\begin{bmatrix} \sigma_{rr} \\ \sigma_{\theta\theta} \\ \sigma_{zz} \end{bmatrix} = [c] \begin{bmatrix} \epsilon_{rr} - \alpha_r \Delta T \\ \epsilon_{\theta\theta} - \alpha_\theta \Delta T \\ \epsilon_{zz} - \alpha_z \Delta T \end{bmatrix} \quad (A2)$$

where  $[c]$  is the matrix of elastic constants, which can be orthotropic. The strains are:

$\epsilon_{rr} = du/dr$ ;  $\epsilon_{\theta\theta} = u/r$ . The axial strain  $\epsilon_{zz} = \epsilon_{zz}^0$ , is independent of  $r$  and usually must be evaluated. Only in the plane strain case is  $\epsilon_{zz}^0$  known ( $\epsilon_{zz}^0 = 0$ ). The axial force,  $F_a = \int_a^b \sigma_z 2\pi r dr$ , is used as a constraint to impose;  $F_a = 0$  or  $F_a = \pi a^2 P_0$ . The boundary conditions are:

$$\sigma_r = 0 \text{ at } r = b$$

$$\sigma_r = -P_0 \text{ at } r = a$$

The program solves the above equations by a finite element method, based on the principle of virtual work. As noted above, orthotropic materials used in axially symmetric fashion for the tube can be incorporated. Any number of materials can be used.

For isotropy  $\alpha_r = \alpha_\theta = \alpha_z = \alpha$

$$[c] = E/(1 + \nu)(1 - 2\nu) \begin{bmatrix} 1-\nu & \nu & \nu \\ \nu & \nu & \nu \\ \nu & \nu & 1-\nu \end{bmatrix}$$

The results obtained (so far) are for 2.5 to 7.5 mm liner in steel.

Caliber	75mm	(a = 37.5 mm)
Wall	25mm	(b = 62.5 mm)

Case 1 - liner is  $\text{Al}_2\text{O}_3$

Case 2 - liner is SiC

For steel	$E = 210 \text{ GPa}, \nu = 0.3$ $\alpha = 11.7 \times 10^{-6} \text{C}^{-1}$
-----------	--

For $\text{Al}_2\text{O}_3$	$E = 400 \text{ GPa}, \nu = 0.25$ $\alpha = 8 \times 10^{-6} \text{C}^{-1}$
-----------------------------	--

For SiC	$E = 420 \text{ GPa}, \nu = 0.2$ $\alpha = 4 \times 10^{-6} \text{C}^{-1}$
---------	---

## Appendix II

### Shrink Fitting Strategy

One of the difficulties concerned with shrink fitting of ceramics is the tendency for local line contacts that lead to tensile stress (c.f., Fig. 12). Such stresses can cause liner cracking. In order to alleviate such problems, an adequate shrink fitting strategy must be established. For present purposes one approach would involve emplacing a thin layer of Ni or Nb between the ceramic liner and the jacket. These materials both have quite high melting temperatures and are relatively soft and ductile. The ductile layers could be in the form either of thin electrolytically deposited layers (Ni) or of thin sheet.

The shrink fit stresses are strongly influenced by the relative liner thickness, as well as the more obvious effects of thermal expansion and interference fit. The initial stress may thus be adjusted over a broad range, given the material properties of the liner and jacket.

### Appendix III

#### Thermal Stresses In Thin Liner

When the liner is thin, the temperature profile (Fig. 7) can be approximated by assuming that the liner is subject to a radial temperature drop,  $T_i - T_o$ , while the jacket is at a constant temperature  $T_o$ . A simple approximation for the stress can then be generated. In the absence of a jacket, the stresses in the liner would be:

$$\sigma_{\theta\theta} \equiv \sigma_{zz} = -E_c \alpha_c (T_i - T_o) / 2(1 - \nu_c)$$

at the bore and

$$\sigma_{\theta\theta} \equiv \sigma_{zz} = E_c \alpha_c (T_i - T_o) / 2(1 - \nu_c)$$

at the outer diameter of the liner, where  $\alpha$  is the thermal expansion coefficient,  $E$  is Young's modulus,  $\nu$  is Poisson's ratio and the subscript  $c$  refers to the ceramic.

In the presence of the jacket, a uniform compression is imposed on the liner, given by;

$$\sigma_{\theta\theta} \equiv \sigma_{zz} = -E_c [\alpha_c (T_i - T_o) / 2 - \alpha_m T_o] / (-\nu_c)$$

where  $m$  refers to the jacket. The net stress on the outer diameter of the liner is thus:

$$\sigma_{\theta\theta} \equiv \sigma_{zz} = E_c T_o (\alpha_m - \alpha_c) / (1 - \nu_c)$$

The stress are thus tensile when  $\alpha_m < \alpha_c$ . A close match in thermal expansion coefficients is thus needed to inhibit liner cracking.

## REFERENCES

1. Vassallo, F.A. 1975. Heat transfer and erosion in the ARES 75mm high velocity cannon. Report No. VL - 5645-D-1. Buffalo, N.Y.: Alvin Calspan.
2. Vassallo, F.A. 1983. Mitigation of heating and erosion in high energy anti-armor automatic cannons. In Proceedings of the 1983 JANAF Propulsion Meeting. Buffalo, New York: Alvin Calspan.

## ACKNOWLEDGEMENT

Drs. C. Levi and R. McMeeking of UCSB attended the workshop, developed the necessary computer software and carried out the calculations in collaboration with R. Mehrabian and A. Evans.

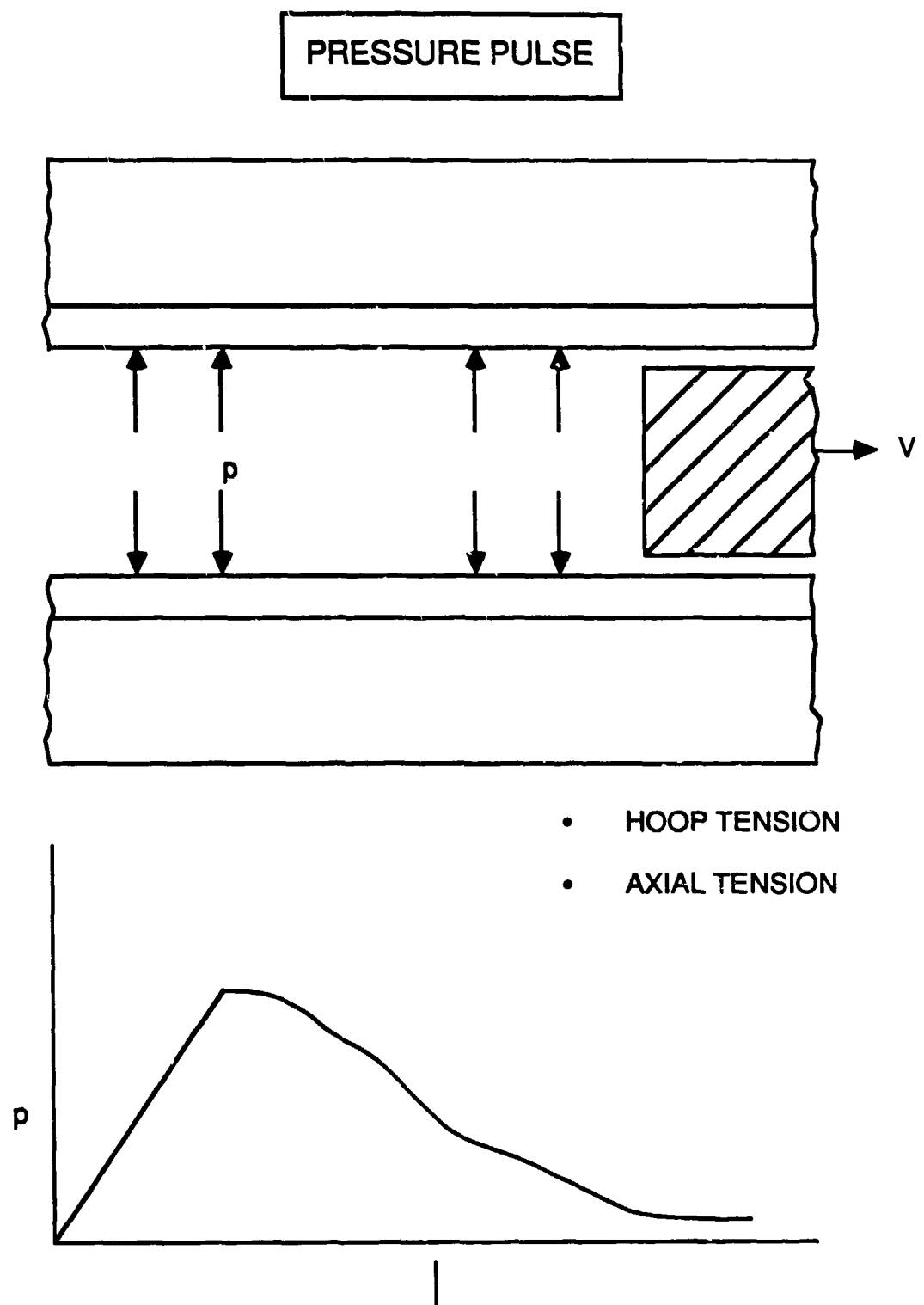


Figure 1. A pressure profile in the bore behind the projectile.

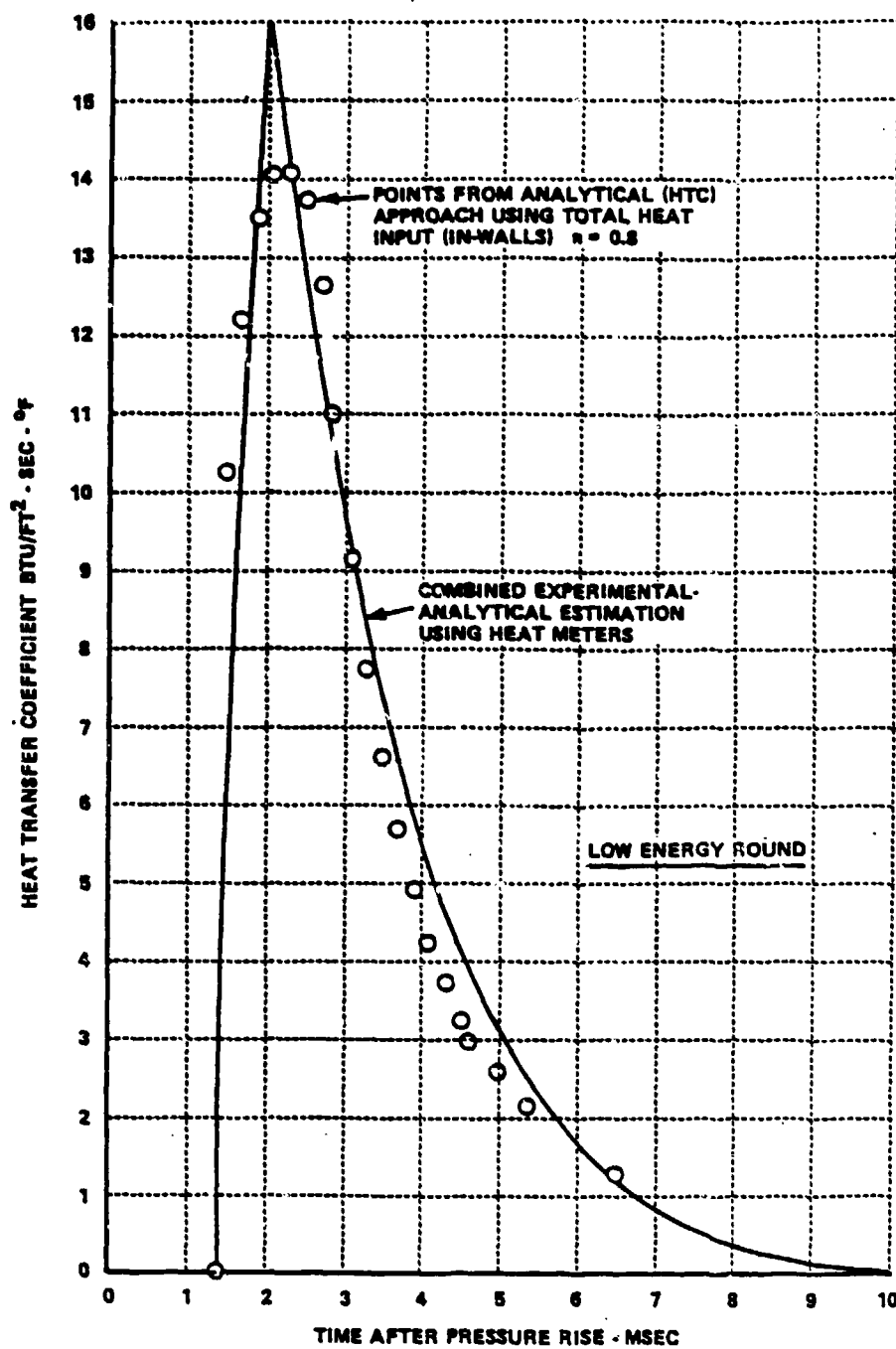


Figure 2. Heat transfer coefficient at 1.5 in. into short barrel (from Ref. 1).

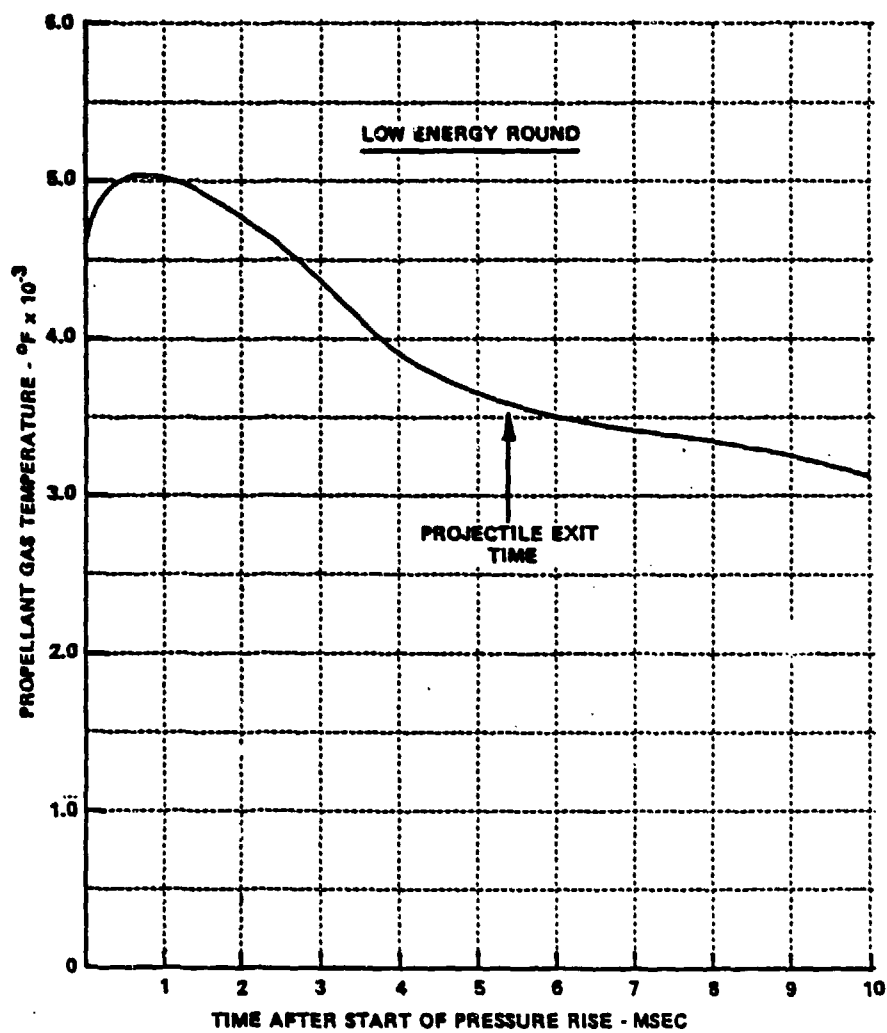


Figure 3. Gas temperature history 75MM cannon (from Ref. 1).

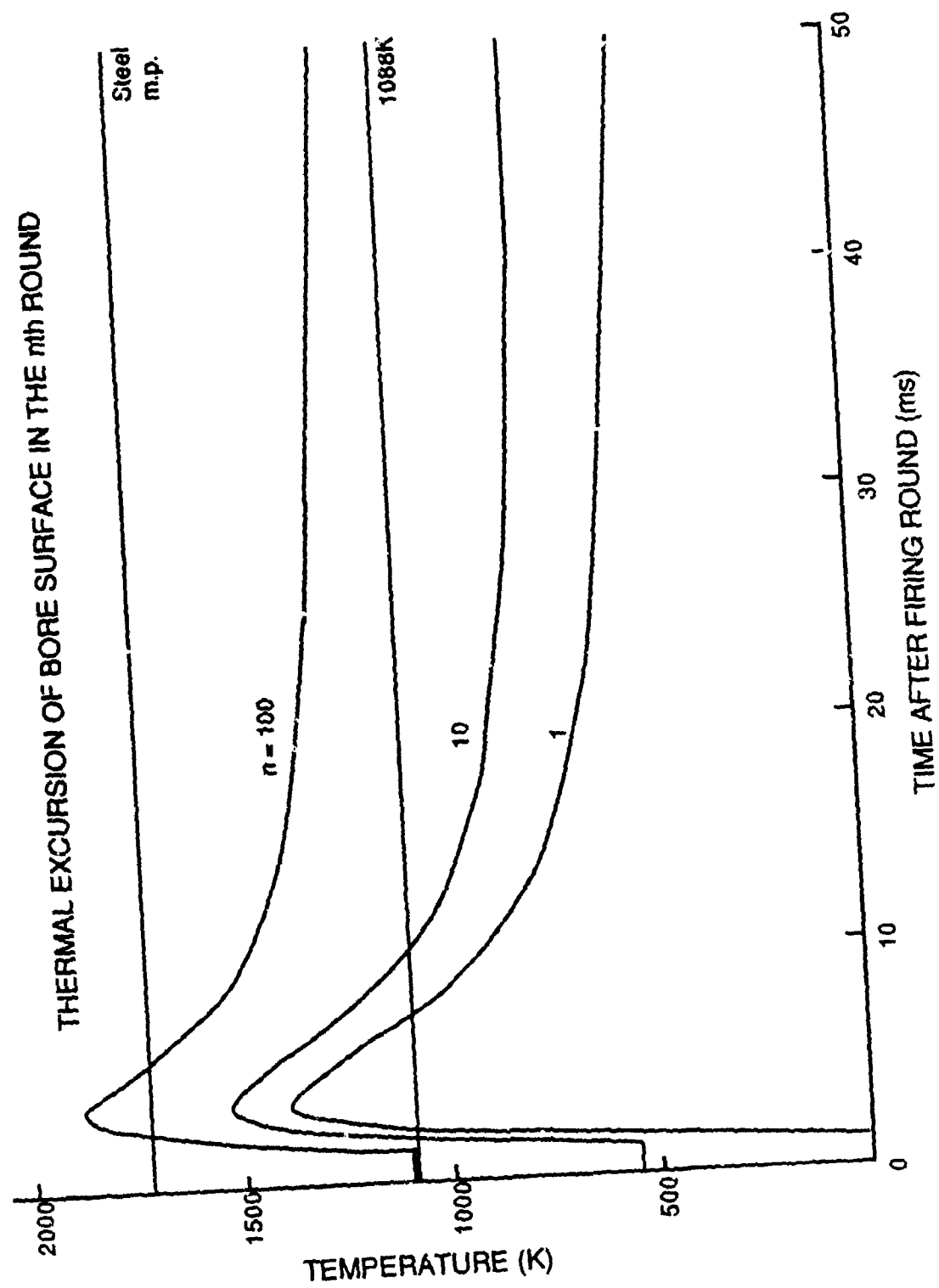


Figure 4. Trends in bore surface temperatures with time for steel barrel.

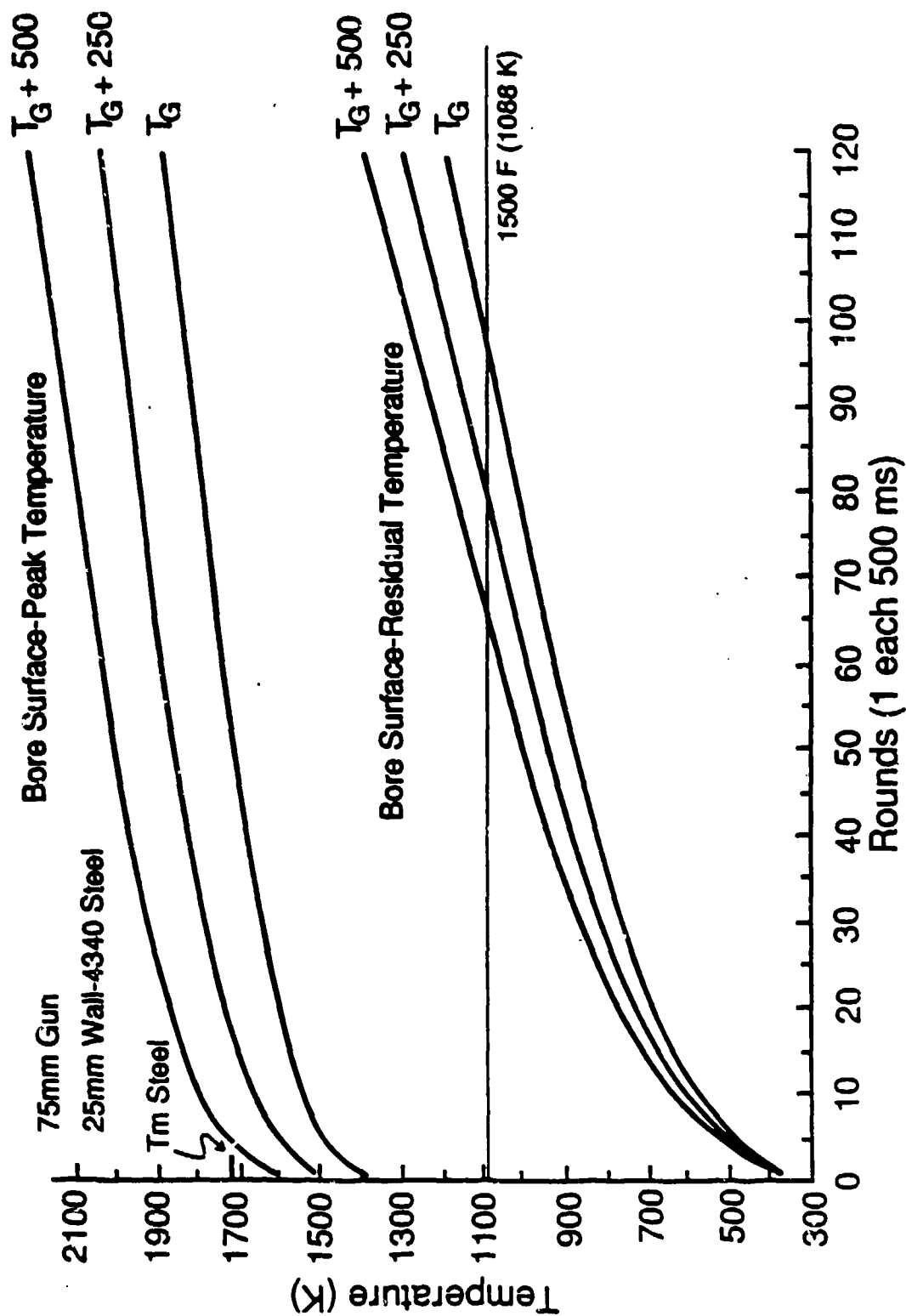


Figure 5. Loci of the bore peak and residual temperature, indicating the effect of increasing the propellant temperature on the bore surface temperature.

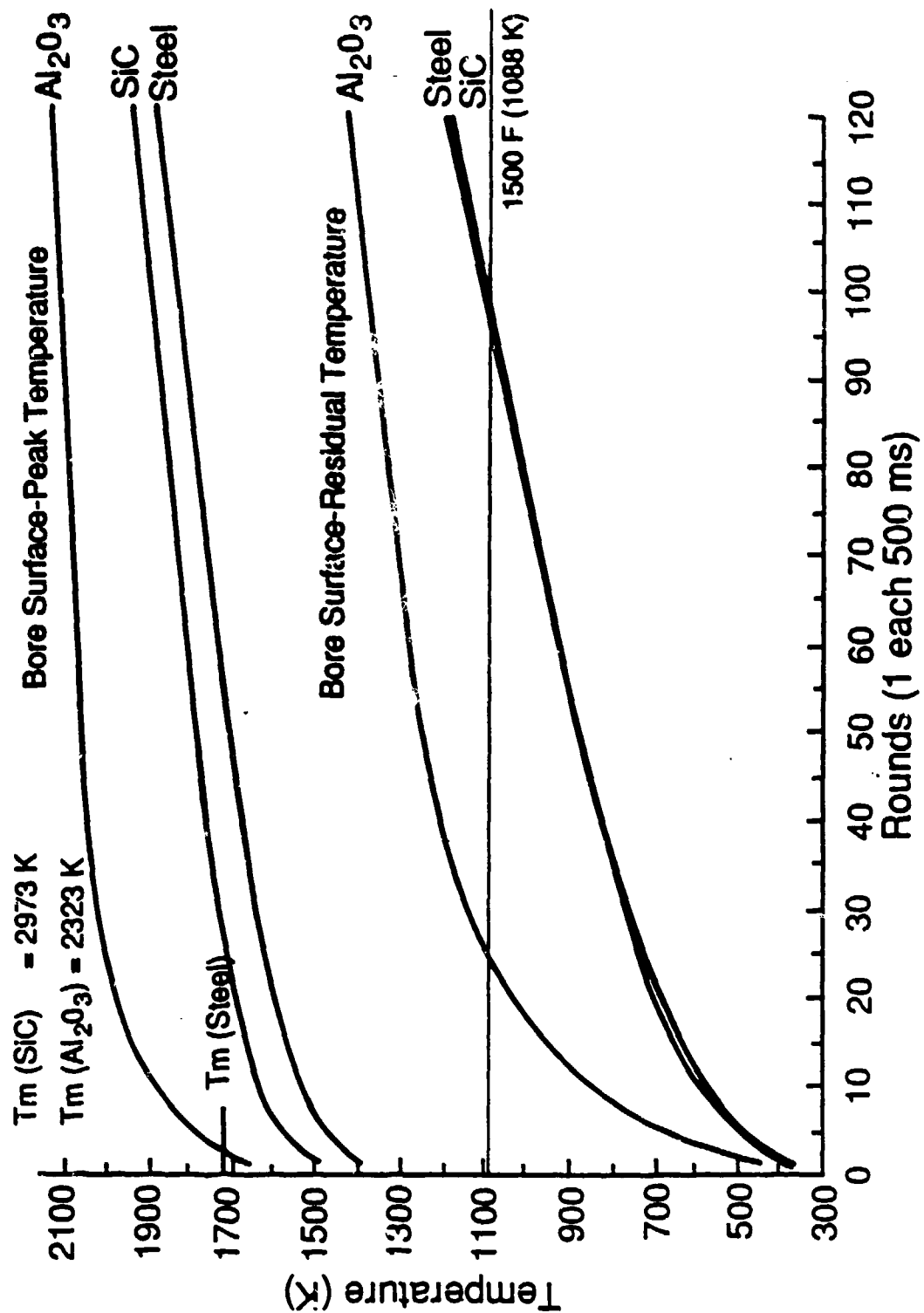


Figure 6. Trends in peak and residual bore system temperature for steel, SiC and  $\text{Al}_2\text{O}_3$ .

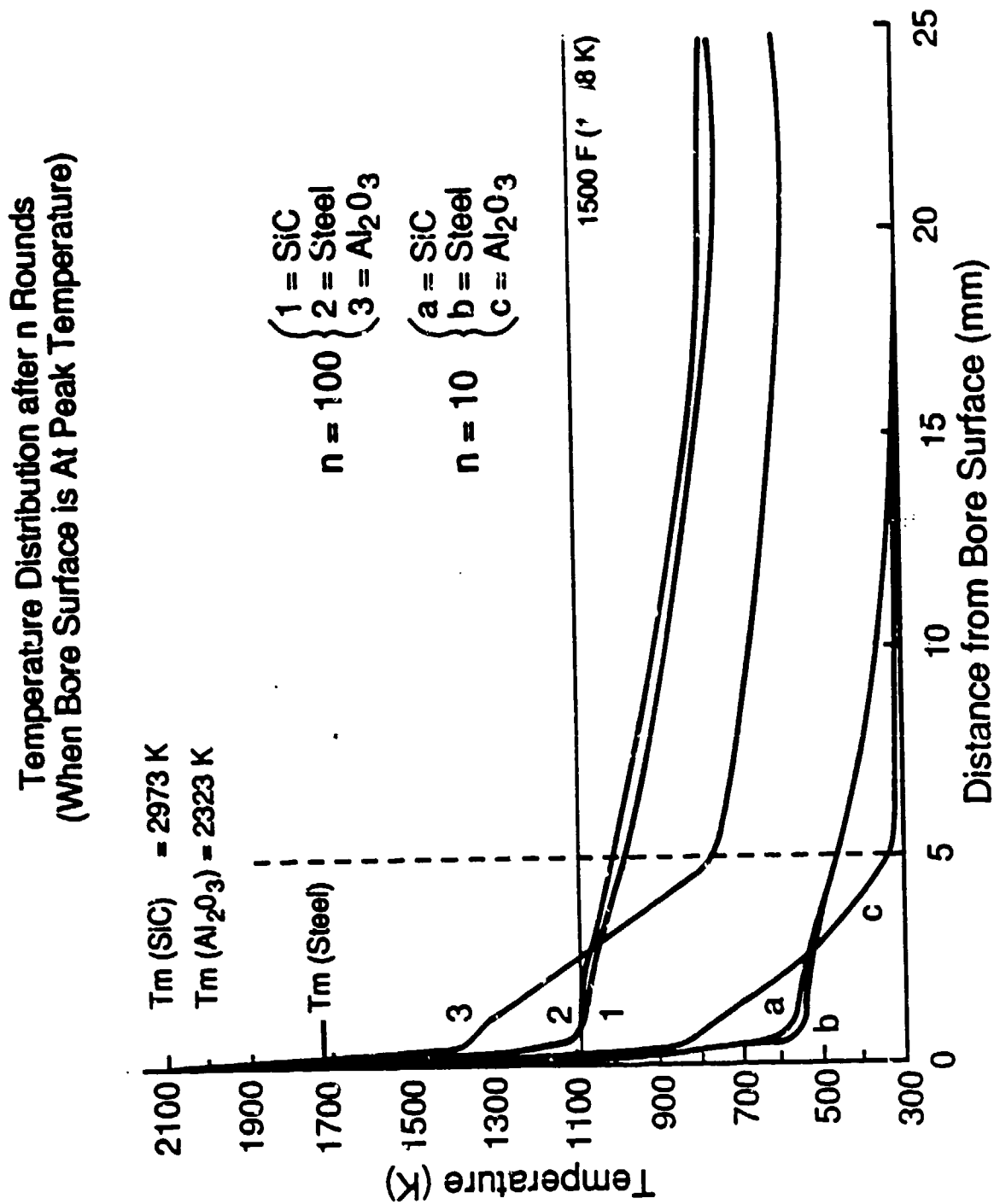


Figure 7. Radial temperature distributions for steel, SiC and  $\text{Al}_2\text{O}_3$ : n is the number of shots.

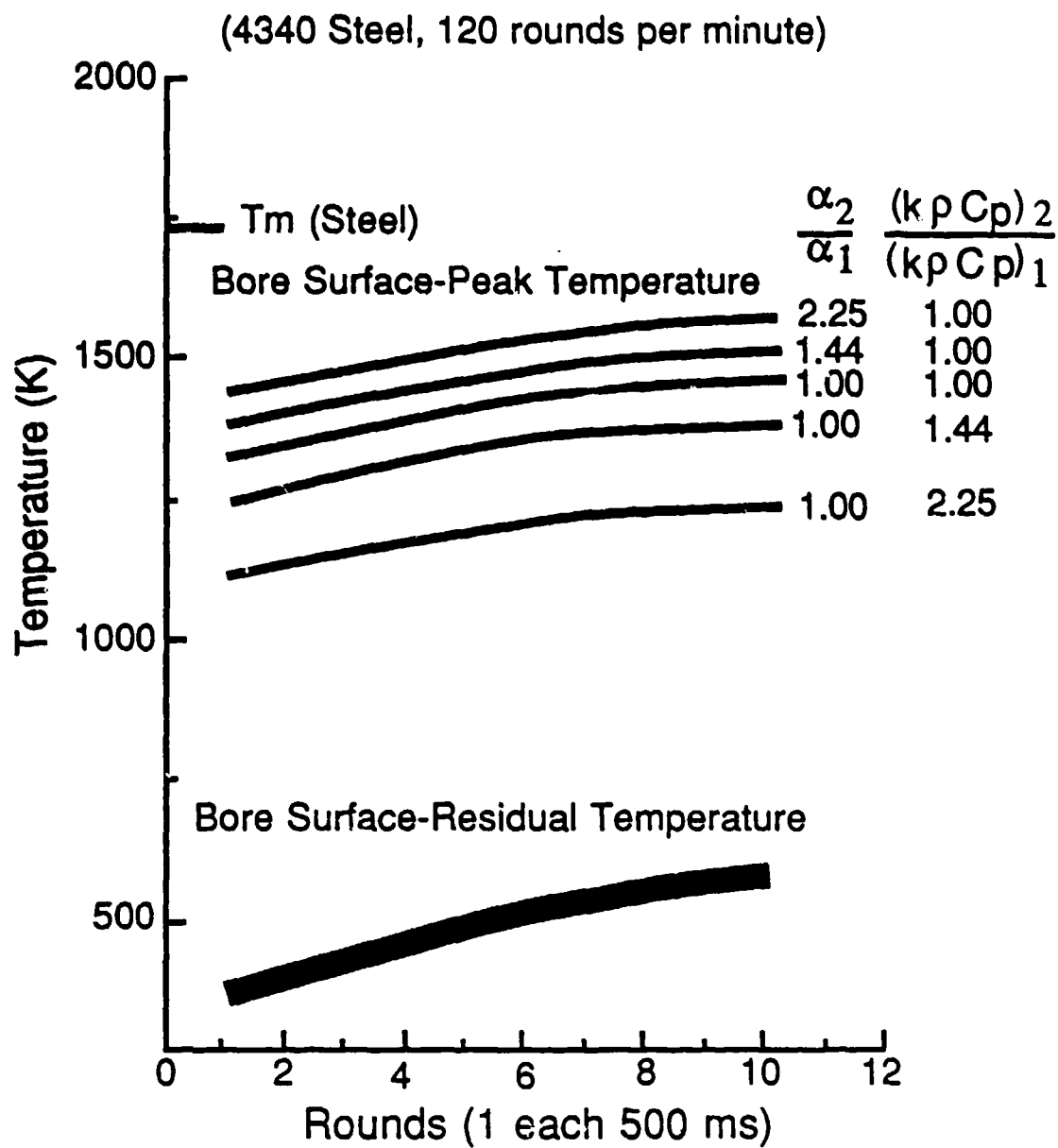


Figure 3. Trends in peak bore temperature with heat diffusivity,  $kpC_p$ .

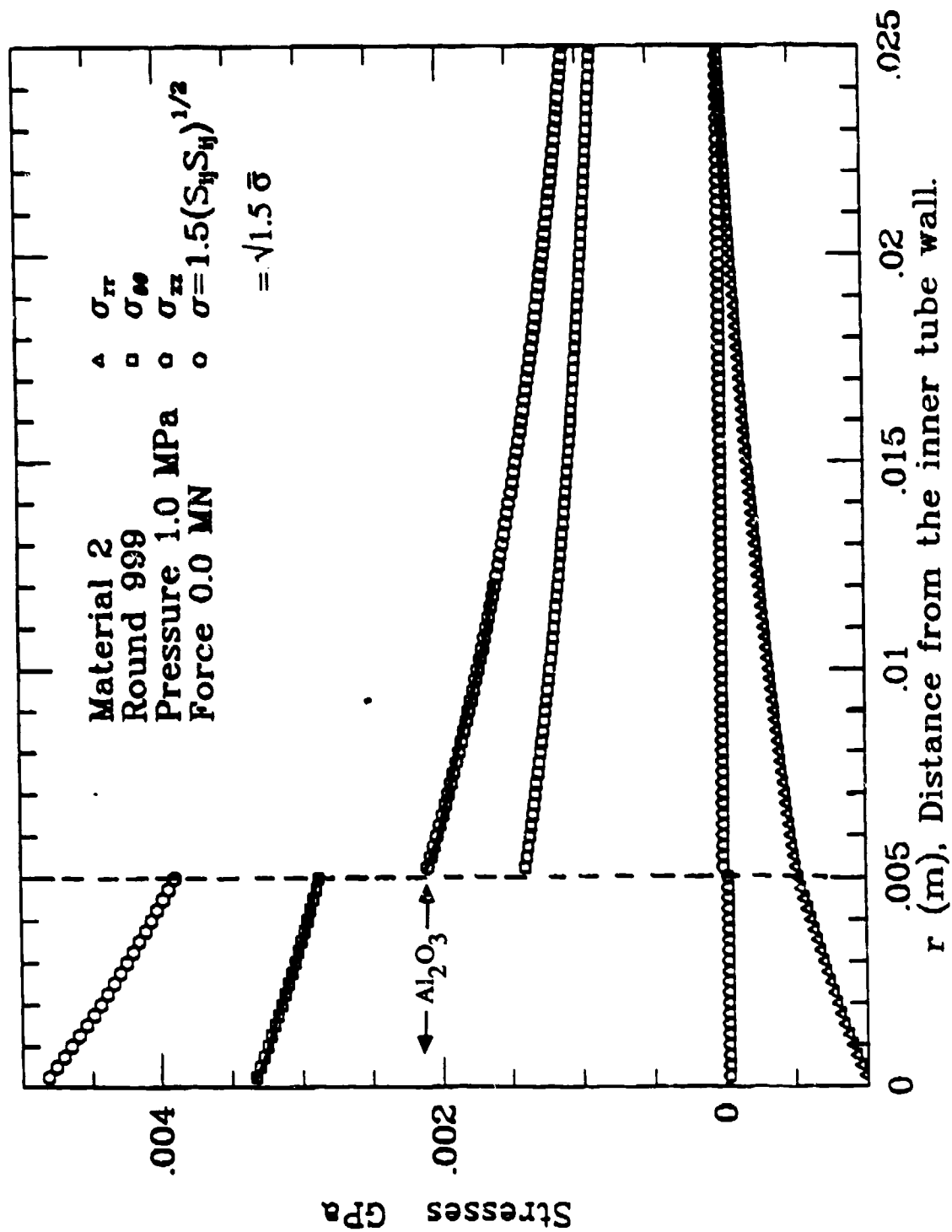


Figure 9. Pressure induced stress in  $\text{Al}_2\text{O}_3$  lined systems.

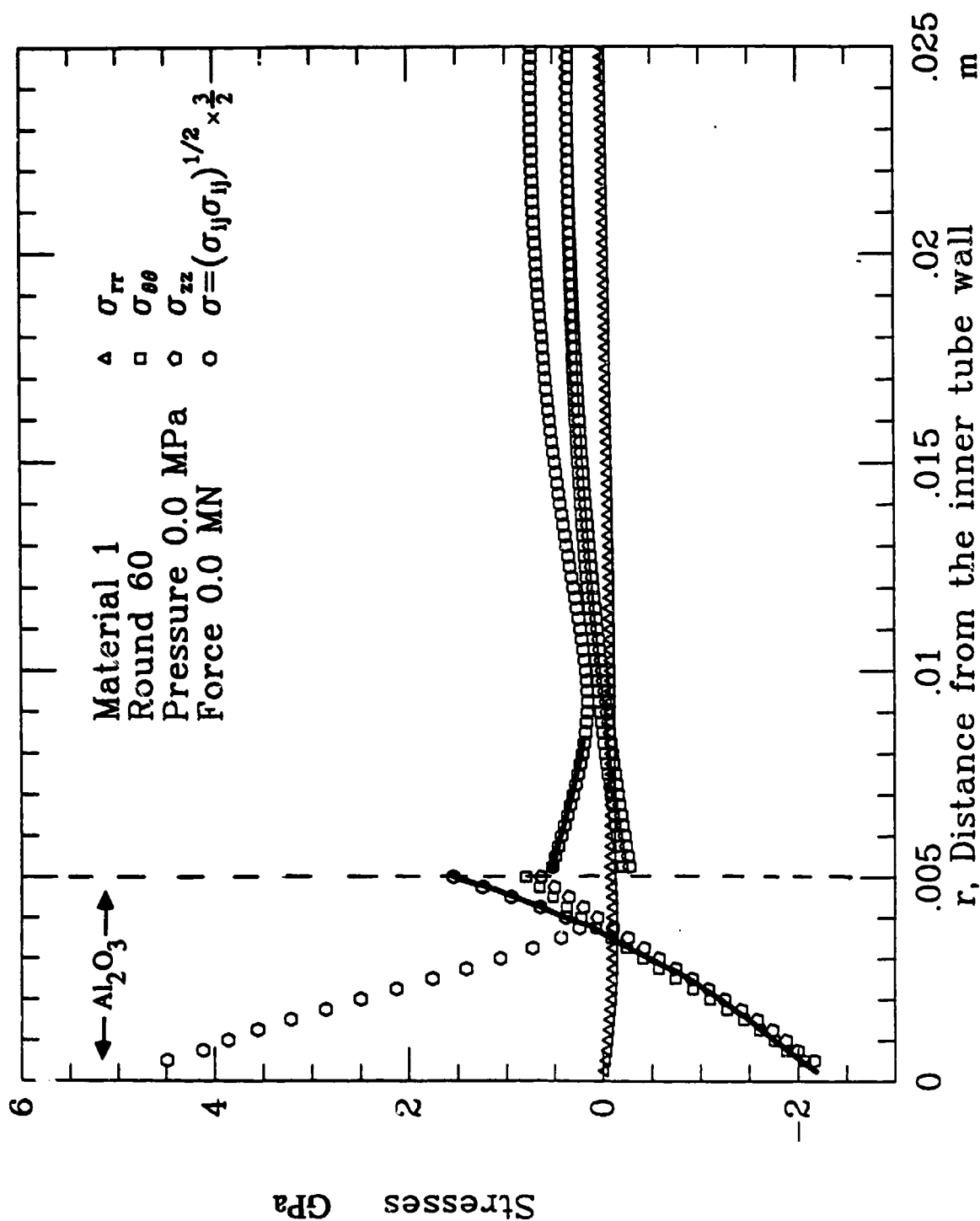


Figure 10a. Trends in thermal stress from bore heating in  $\text{Al}_2\text{O}_3$ .

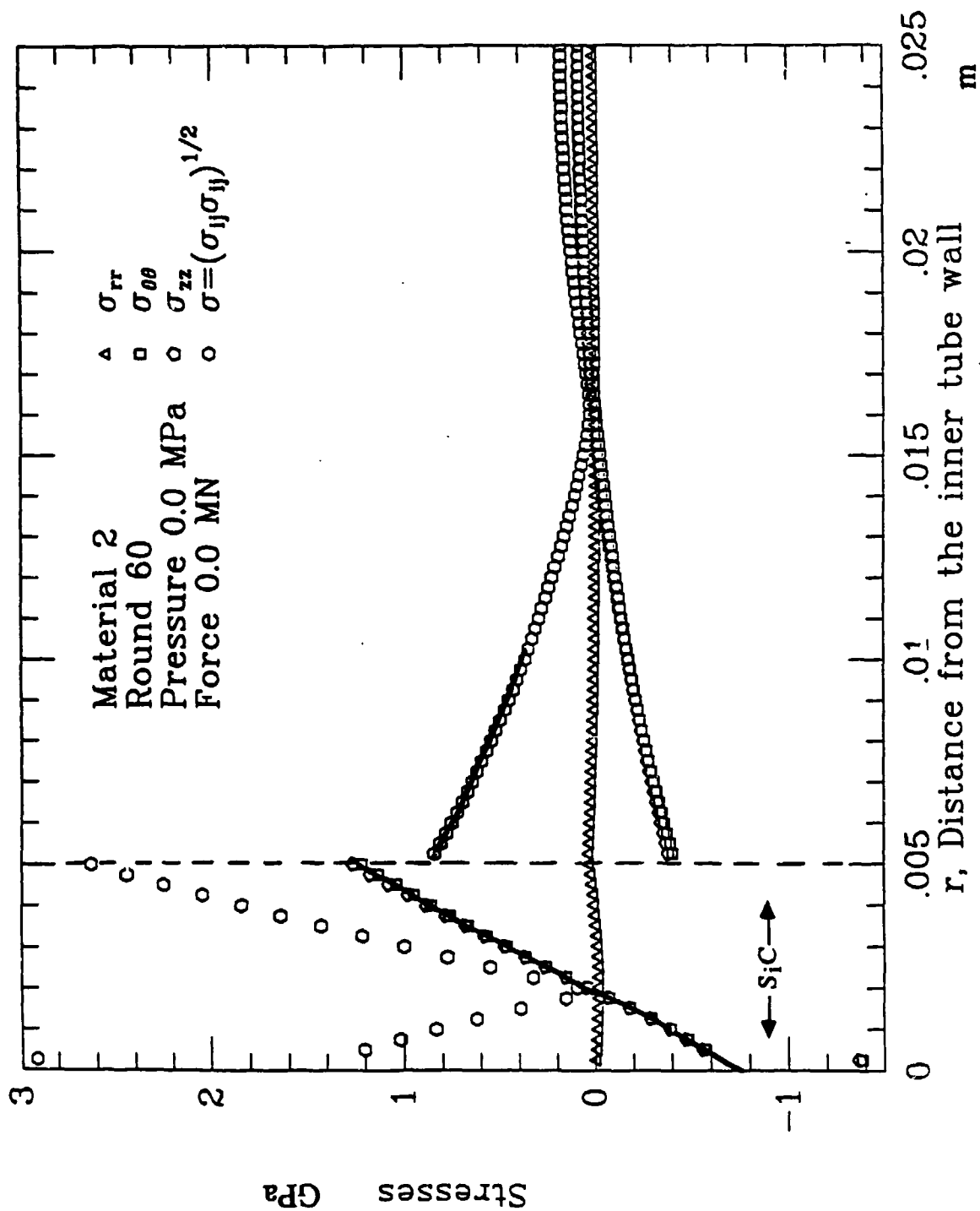


Figure 10b. Trends in thermal stress from bore heating in SiC liners.

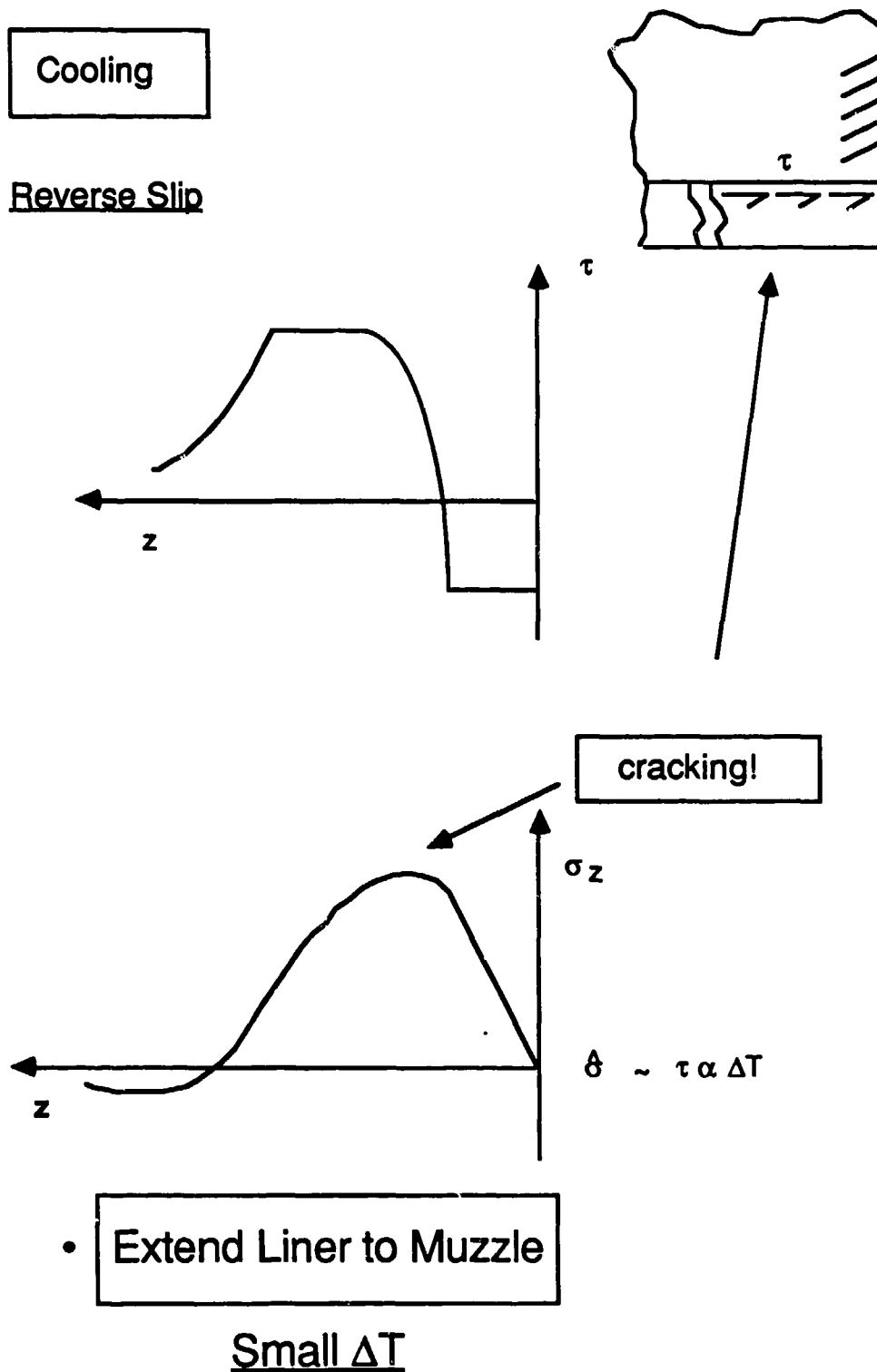


Figure 11. Axial tensile edge stresses created by thermal cycling.

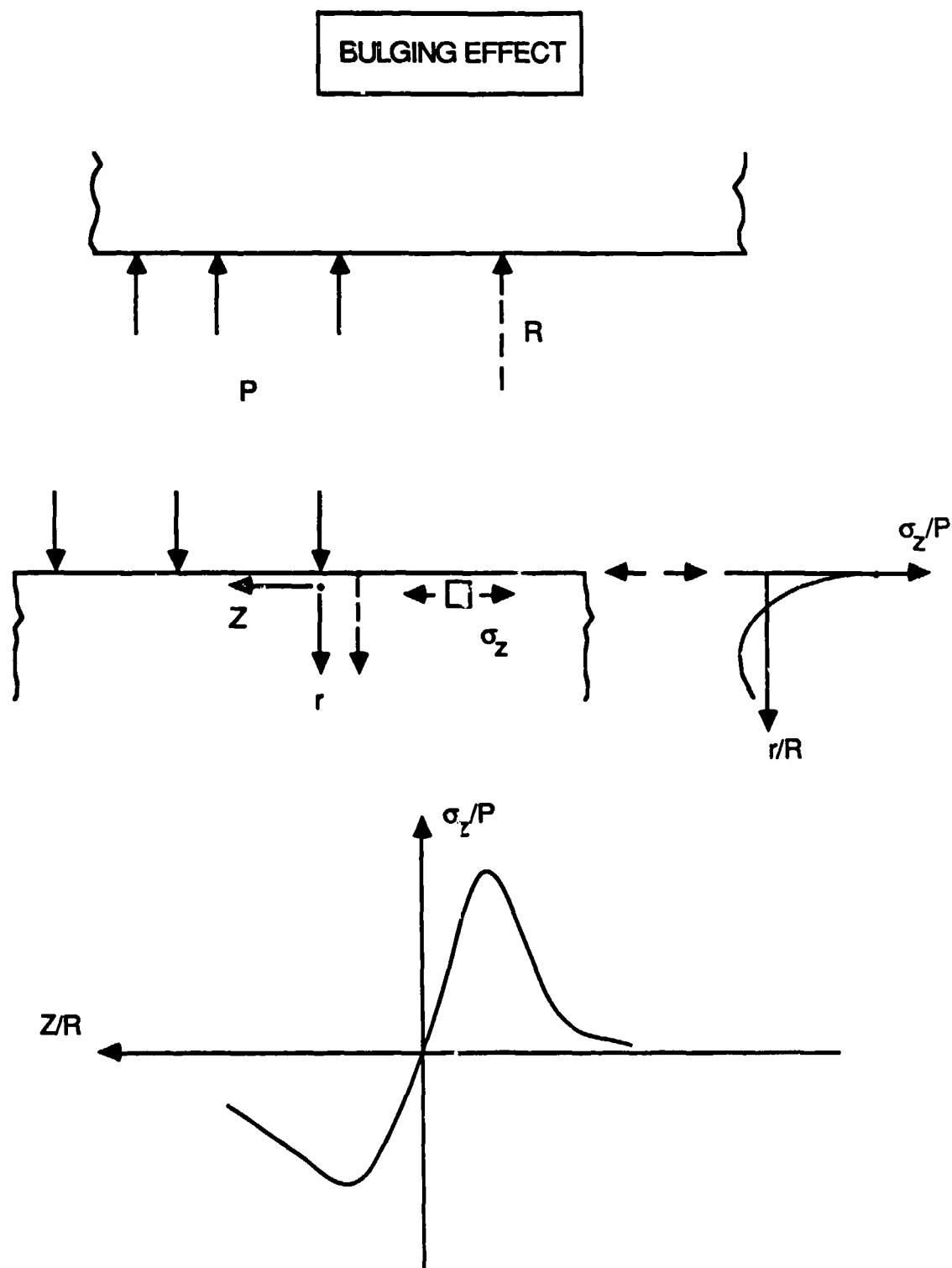


Figure 12. Bulging induced axial tensile stresses at the end of the pressure pulse.

## COMMENTS ON GUN BARREL SYSTEMS

G. M. Whitesides

The recent discussion of advanced gun barrel systems raised a number of interesting questions concerning the performance and operation of existing barrel systems. This memo is to raise several questions concerning these existing systems and to offer an opinion that the study of these existing systems - - especially the mechanisms of erosion occurring in their use - - would be highly relevant to minimizing potential erosion in the proposed advanced system and potentially immediately very useful in extending the life and performance of existing conventional systems. I suggest the following opportunities for research in this area:

1) Retrospective analysis of failed, eroded conventional barrels. The topics of interest would include the composition of the inner barrel surface in eroded and non-eroded regions, particularly using the techniques of modern vacuum physics (XPS, RBS, SIMS, metallurgical microanalysis, neutron activation analysis). The objective of this work would be to try to infer the chemical reactions that had occurred in the erosion processes. Was nitriding important? Carbiding? Oxidation? Is there evidence for abrasive scoring? Melting? How firm is the evidence for chemical erosion by hot reactive gas streams?

2) Examination of the chemistry of explosive flames. Here, it seems relevant to examine both new, high-energy systems and the current low-energy systems. A range of techniques have been developed that may be useful in this field, ranging from current research in combustion and flame chemistry to the analytical techniques developed to study particulate and hot gas erosion in magnetohydrodynamics and around gas turbine blades. I, personally, believe that it would be possible to develop a very useful model system for explosive flames based on a high velocity gas with variable temperature,

composition, and gas velocity. I regard the assertions in the workshop to the contrary as being the usual restatement of the fact that it has not been done in the past. I would suggest a study of hot gas corrosion using these gas model systems comparing steel, stellite, and candidate ceramics. I do not see much reason to develop ceramics that are going to be corroded, and I do not believe that the evidence that, silicon nitride does not corrode, as being convincing. The hope in this enterprise would be that, by understanding this hot gas corrosion, it might be possible either to modify the barrel surface (or, perhaps, the flame) to minimize corrosion. I suggest that there may be fundamentally different problems for metal and ceramic barrels. In particular, I suspect that oxidizing flames are more corrosive toward metal barrels, and reducing flames toward ceramic barrels. It is not at all clear that explosive systems optimized for metals will be equally good for ceramics. The types of questions that one would like to ask are: Should the flame be oxidizing or reducing? Should it be rich in nitrogen oxides or poor? What about CO (which can reduce metal oxides to metals)? How important are halogens and sulfur impurities?

3) There was an assumption in the meeting that mechanics were more important than chemistry in determining the performance of gun barrels. I don't dispute the fact that mechanics are very important, but it is not obvious to me that chemistry is not equally important in erosion, initiation of stress corrosion cracking, and even conditioning metal for creep at high temperatures. Both thermochemistry and thermal mechanics must be considered together, to avoid unsatisfactory conclusions.

4) It would seem a very attractive enterprise to develop sensors specifically for the environment and time scale appropriate to a gun barrel. It seems to me that fiber optics, flash X-ray, and retrospective surface analysis on the barrel or on test patches introduced into the barrel (perhaps in the relatively protected environment of the rifled groove) and would lead to useful information. The Los Alamos talk, in particular,

suggested that it should be very easy to obtain in-flight information about bullet-barrel interactions. I also suspect that a detailed acoustic analysis could be very helpful in understanding energy deposition in the barrel. This may be particularly important in the ceramic barrel, where reflection from the ceramic end pieces is critical.

5) The ceramic barrel will depend upon a very demanding job of heat shrink fitting. It would seem that a program to develop materials specifically for the sleeve in a shrink fit is an appropriate problem: acoustic matching and damping at the ends and edges of the ceramic piece and ductile materials intended to avoid local pressure points on the ceramic are both important targets.

6) I was particularly interested by the opportunities for chemistry and materials in the rotating band. This is one component of the system that, I suspect, can be changed relatively easily. I gather that it is now considered relatively non-functional - - it simply provides a pressure seal for gases and contributes to locking the projectile into the rifling. I would propose using the rotating band both as a sensor system and also, more attractively, as a functional part of the gun system. It could, in principle, add protectants, ablate or volatilize and donate components to a gas phase stream that would inhibit oxidation or moderate and control flame chemistry, replace important components on the eroding barrel surface, or act as a sensor for the entire firing process. It seems to me that the testing of materials for the rotating band with lubricating, organometallic, or other components might provide a minimum - change method for modifying the characteristics of existing gun systems. I suspect that the amount of imaginative chemistry/materials science that has been devoted to the rotating band in, particularly, small-caliber guns has been limited.

Each year at the summer conference, in order to develop communications and interchanges between DARPA personnel and the Council members, a series of presentations are made by both groups in a joint meeting. The following agenda shows the speakers and some of the topics discussed on July 7, 1987.

AGENDA

DARPA-MRC PRESENTATIONS

July 7, 1987

Tuesday, July 7, 1987

Reynolds, Roosild, Wilcox - Overviews

Patten - Eye Protection from Pulsed Lasers

Farnum - Gun Barrels

Rhyne - High Temperature Superconductors

Murphy - Electronic Materials Packaging

Neff - Optical Symbolic Computing

Yariv, McGill, Stilck, Whitesides, Evans, Osgood - Research Interests and Direction

These presentations are used to acquaint the DARPA personnel with the activities of some of the MRC members and the converse exchange.

## ATTENDEES

### MRC MEMBERS

Budiansky  
Dresselhaus  
Evans  
Hirth  
Margrave  
McMeeking  
Osgood  
Stille  
Williams  
Sinnott

Cross  
Ehrenreich  
Ferry  
Hutchinson  
McGill  
Mehrabian  
Ros  
Whitesides  
Wrighton  
Yariv

### DARPA

Reynolds  
Roosild  
Wilcox  
Patten  
Farnum  
Rhyne  
Murphy  
Neff  
Prabhakar  
Parrish

AGENDA  
DIAMOND-LIKE MATERIALS

July 8-10, 1987

Wednesday, July 8 PM

Introductory Remarks - J. L. Margrave, MRC/Rice Univ.

"Synthetic Diamonds" - R. DeVries, GE

"Synthesis and Characterization of CVD Diamond-Like Films" - K. Spear, Penn. State

Thursday, July 9

"The Commercialization of CVD Diamond Technology" - M. Pinneo, Crystallume

"Preparation and Uses of Diamond-Like Materials" - T. Nakahara, Sumitomo Electric Ind.

"Dense Diamond-Like Hydrocarbon Films" - J. C. Angus, Case Western Reserve

Friday, July 10

"Electronic Devices from Diamond Films" - M. Geiss, MIT Lincoln Labs.

"Summary: Speculation and Extrapolation" - G. Whitesides, MRC/Harvard

Brainstorming Session

# DIAMOND CONFERENCE

July 8, 1987

<u>NAME</u>	<u>AFFILIATION</u>	<u>TELEPHONE</u>
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Nakahara, T.	Sumitomo Electric Ind.	Japan 06-461-1031
Matsuo, M.	Sumitomo Electric Ind.	213-373- 8493
Prabhakar, A.	DARPA/DSO	202-694-3145
Roosild, S.	DARPA/DSO	202-694-3145
Schriemph, T.	Physical Sciences Inc.	703-548-6410
Patten, F.	DARPA	202-694-1303
Ehrenreich, H.	Harvard/MRC	617-495-3213
Hirth, J.	Ohio State U /MRC	614-292-0176
Reynolds, D.	DARPA	202-694-3145
Sinnott, M.	Mich/MRC	313-764-4314
Camahan, B.	Mich/MRC	313-764-3366
Wilcox, B.	DARPA	202-694-1303
Hucke, E.	Mich/MRC	313-764-3302
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Ferry, D.	Arizona St. Univ./MRC	602-965-3708
McGill, T.	Caltech/MRC	818-356-4849
Osgood, R.	Columbia/MRC	212-280-4462
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Berry, M.	Rice Univ./HARC	713-527-8602
Cross, L.E.	Penn State/MRC	814-865-1181
Spear, K.	Penn State	814-865-4992
Stille, J.	Colo. State Univ./MRC	303-491-7602
Ross, J.	Stanford Univ./MRC	415-723-9203
Williams, J.	Carnegie Mellon/MRC	412-268-2477
Pinneo, M.	Crystallume	415-494-0660
Ravi, K.V.	Crystallume	415-494-0660
Kaae, J.L.	G.A. Technologies	619-455-2957
Angus, J.	Case Western Reserve	216-368-4133
Geis, M.	MIT/Lincoln Labs.	

- EXECUTIVE SUMMARY -  
CVD DIAMOND AND DIAMOND-LIKE MATERIALS

J. L. Margrave

**OBJECTIVES OF THE WORKSHOP**

The workshop was organized with the goal of developing an understanding of the current state of the CVD-Diamond and Diamond-Like film technology and exploring potential applications in DoD.

There were several presentations, including an historical overview of diamond synthesis research; A summary of two American research programs -- Penn State and Crystallume; a report on CVD diamond research at Sumitomo Electric in Japan; a review of "Diamond-Like" film production and uses including US, Japanese and other research; a discussion of the applications for diamond slabs, diamond films and fluorinated diamond surfaces in solving various lubrication and wear problems; and a summary of the current state-of-the-art in using diamonds for electronic devices. These presentations were followed by an overview of the field and a lively discussion of the achievements and problems in bringing CVD diamond out of the research lab and into production.

**DOD RELEVANCE**

Many areas of DoD relevance were identified:

1. High-power microwave amplifiers
2. Power transistors
3. High-temperature electronics in hostile environments
4. Hard, erosion-resistant, transparent coatings
5. Heat sinks
6. Optics for high-power lasers

7. Cutting tools and drill bits
8. Bearings and other tribological applications

### TECHNICAL SUMMARY

Diamond in many senses is the ultimate material and chemical vapor deposition techniques open up hundreds of opportunities for applications. There are now almost thirty years of literature in this field and successful growth of diamond-like amorphous films (with appreciable hydrogen content) and crystalline diamond films (with very low hydrogen content) are widely reported. In most cases, an  $H_2/CH_4$  mixture is dissociated (hot filament, RF or microwave discharge, laser, etc.) to produce excited  $C_x$  and  $CH_x$  species which lead to diamond growth on suitable substrates or crystalline diamond seeds. Thicknesses of films up to  $25\mu$  have been prepared at deposition rates of  $\sim 1000$  Å/hr.

In spite of the ease of producing diamond films and the many examples of potential commercial applications, there are many unanswered questions and concerns relating to

1. The details of the nucleation process, kinetics of growth and exact mechanism of deposition are not known. Films deposited on various substrates are usually polycrystalline and may appear grayish because of graphite inclusions. Although all of the growth systems basically use the same chemistry (a hydrogen plasma with a small amount of methane), it is not clear which plasma species ( $CH_3$ ,  $CH_2$ ,  $CH$ ,  $C_2H_2$ ,  $C_2H$  or even oxygenated versions of these) contribute predominantly to the CVD film growth.
2. All of the researchers agree that H-atoms play a unique role, probably as a graphite remover. It is not clear whether traces of oxygen or nitrogen are good or bad.
3. Biasing of the substrate to attract ionic species also seems effective. In the extreme, ion sputtering methods have been used to achieve diamond film growth.

4. Techniques for growing doped crystals are not well understood. Controlled doping of diamond films with N, P or As or with B, Al or Ga has not yet been accomplished.

5. Techniques for growing essentially defect-free, crystalline diamond films of reasonable thickness (5-100 $\mu$ ) in reasonable times (1000-10,000 Å/hr) on selected substrates are being developed but may be 1-3 years away.

6. Significant growth of high-quality diamond crystals still requires a diamond seed.

### FOREIGN COMPETITION

In this field it is clear that the US competitive position is precarious at best. Russian work in this field dates back at least fifteen years but there is limited knowledge of their exact recent achievements.

Japanese scientists/engineers have been aggressively researching in this area for over a decade and their early successes in growing macro-films were reported by 1983. Based on the literature and the enlightening presentation by Dr. T. Nakahara of Sumitomo Electric Industries, it is clear that Japanese researchers have achieved:

1. The only successful techniques for doping diamonds (p-type with B; n-type with P)
2. The best CVD-technology for growing crystalline diamond films
3. Epitaxial growth of diamond films on selected substrates
4. Techniques for large scale production of products utilizing diamond/ diamond-like films

Further, with the withdrawal of GE from the field, it appears that Japan, the USSR and South Africa are the only sources of large diamond crystals of the sort needed for heat sinks and for diamond electronics. This will be a great disadvantage to US exploitation/use of diamond-based technology.

## **SUMMARY**

Diamond has unique properties which make it attractive for many practical applications:

- High-temperature semiconductor devices
- IR/VIS/X-ray windows
- Audio speaker diaphragms
- Heat sinks
- Anvils, drill bits
- Cutting tools

The low cost starting materials ( $\text{CH}_4$  and  $\text{H}_2$ ), simple activation methods (hot filaments, RF or microwave discharged), and convenient reproducibility of film growth techniques would indicate a brilliant future for CVD diamond technology on a world-wide basis. Science/imagination/financial support are the limiting parameters.

In recognition of the rapid developments of pertinent technology in this field, DARPA should:

1. Encourage the development of large-scale applications of diamond-like coatings. There are many areas where this hard, erosion-resistant material can solve real problems:

Anti-reflection Films

Inorganic Resists

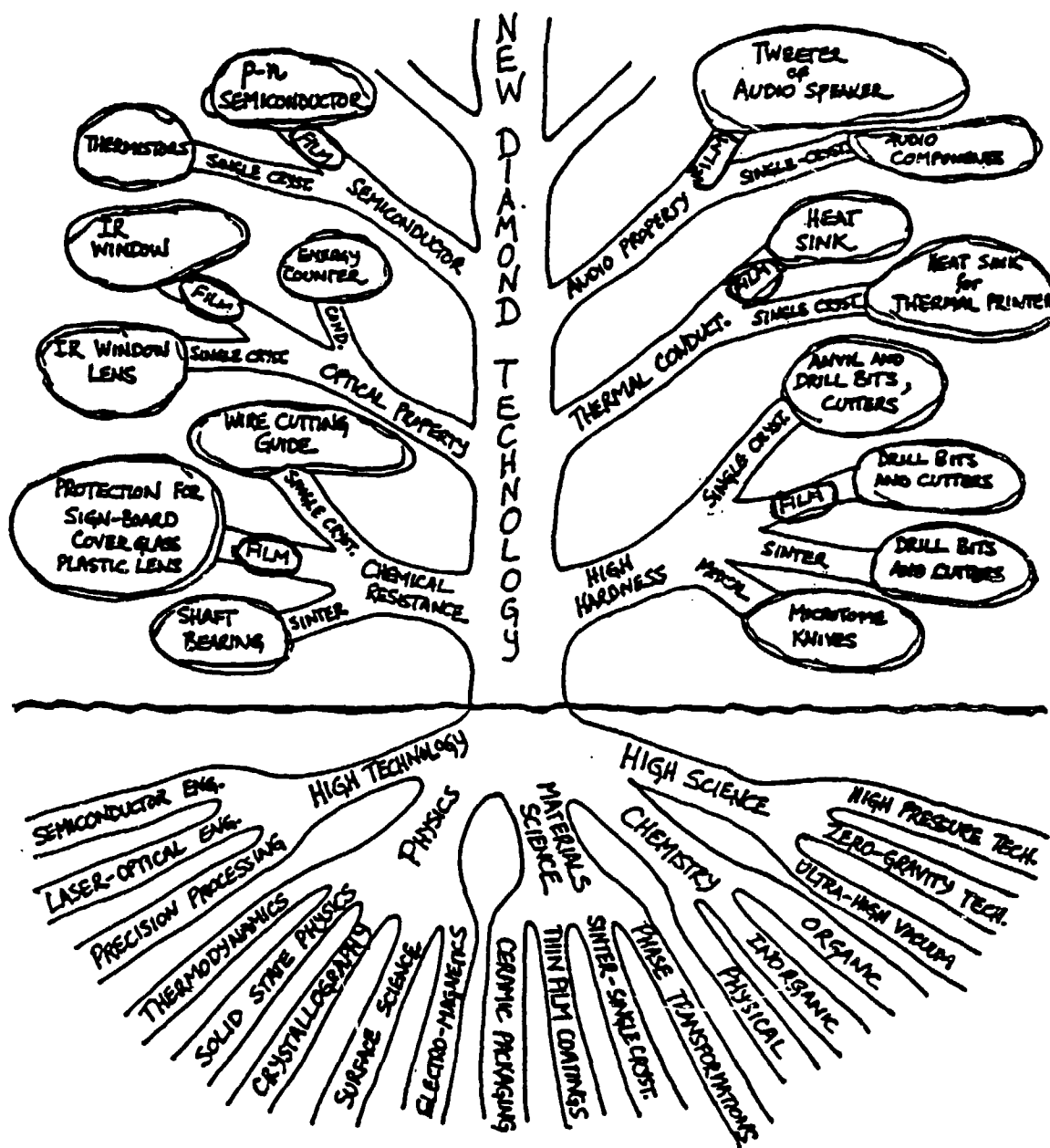
Computer Disc Protective Coating

Audio Diaphragms and Cones

2. Provide support for developing full-scale production facilities for diamond film, but only after the fundamental aspects of the nucleation/kinetics of growth are understood.
3. Actively support materials characterization research programs related to

diamond electronics. Doping and annealing are two areas of concern. Essentially defect-free, high purity crystalline diamond films are needed.

4. Protect/develop US supplies/sources of large synthetic (high-pressure) diamonds for use as heat sinks and in electronic devices.



from Bulletin Ceramic Society of Japan  
September-November 1988

## CVD DIAMOND WORKSHOP

J. L. Margrave, L. E. Cross, M. S. Dresselhaus, T. C. McGill, R. M. Osgood, J. K. Stille

Approximately 30 persons participated in the CVD diamond workshop. Overall, the meeting presentations covered an historical overview of diamond synthesis research; a summary of two american research programs -- Penn State and Crystallume; a report on CVD diamond research at Sumitomo Electric in Japan; a review of "Diamond-Like" film production and uses including U.S., Japanese and other research; and a summary of the current state-of-the-art in using diamonds for electronic devices. These presentations were followed by an overview of the field and a lively discussion of the achievements and problems in bringing CVD diamond out of the research lab and into production. New ideas for a discussion of the application for diamond slabs, diamond films and fluorinated diamond surfaces in solving various lubrication and wear problems; using diamond slabs or diamond film are usually based on the exploitation of one of the unique physical or chemical properties. Diamond in many senses is the ultimate material and chemical vapor deposition techniques open hundreds of opportunities for applications.

In spite of these optimistic predictions and examples of commercial applications, there are many unanswered questions and concerns: (1) the details of the nucleation process, kinetics of growth and exact mechanism of deposition are not known. Films deposited on various substrates are usually polycrystalline and maybe appear grayish because of graphite inclusions. Although all of the growth systems using diamond slabs or diamond film are usually based on the exploitation of one of the unique physical or chemical properties. Diamond in many senses is the ultimate material and chemical vapor deposition techniques open hundreds of opportunities for applications.

In spite of these optimistic predictions and examples of commercial application, there are many unanswered questions and concerns:

(1) the details of the nucleation process, kinetics of growth and exact mechanism of deposition are not known. Films deposited on various substrates are usually polycrystalline and may appear grayish because of graphite inclusions. Although all of the growth systems basically use the same chemistry (a hydrogen plasma with a small amount of methane), it is not clear which plasma species ( $\text{CH}_3$ ,  $\text{CH}_2$ ,  $\text{CH}$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}$  or even oxygenated version of these) contribute predominately to the CVD film growth.

(2) All of the researchers agree that H-atoms play a unique role, probably as a graphite remover. It is not clear whether traces of oxygen or nitrogen are good or bad.

(3) Biasing of the substrate to attract ionic species also seems effective. In the extreme, ion sputtering methods have been used to achieve diamond film growth.

(4) Techniques for growing doped crystals are not well understood, controlled doping of diamond films with N, P or As or with B, Al or Ga has not yet been accomplished.

(5) Techniques for growing essentially defect-free, crystalline diamond films of reasonable thickness (5-100 $\mu$ ) in reasonable times (1000-10,000  $\text{\AA}/\text{hr}$ ) on selected substrates are being developed but may be 1-3 years away.

(6) Significant growth of high-quality diamond film still requires a diamond seed.

### Summary

Diamond has unique properties which make it attractive for many practical applications

- High-temperature semiconductor device
- IR/VIS/X-ray windows
- Audio speaker diaphragms
- Heat sinks

-- Anvils, drill bits

-- Cutting tools

The low-cost starting materials ( $\text{CH}_4$  and  $\text{H}_2$ ) simple activation methods (hot filaments, RF or microwave discharges), and convenient reproducibility of film growth techniques would indicate a brilliant future for CVD diamond technology.

# DIELECTRIC PROPERTIES OF CVD DIAMOND FILMS

L. Eric Cross

## General Comments

Considering the lead time of more than four years enjoyed by Japanese researchers in the plasma assisted CVD of diamond, the United States has made excellent progress in producing true diamond films. Clearly, the process differs from that required for CVD graphite primarily in the high concentration of atomic hydrogen which must be generated in the plasma to stabilize the normally metastable diamond structure. It would appear that the "processing window" for diamond production is very restricted and that continuous effort will be required to improve film quality and establish reliable process control. Raman spectroscopy appears to offer an excellent tool for establishing the quality of the diamond films.

## Dielectric Properties

In view of the very high thermal conductivity and excellent insulating character of the type IIa diamond, it is natural to consider the plasma assisted CVD coatings for applications in semiconductor packaging. Reviewing the electrical properties reported by T. Nakahara of Sumitomo Electrical Industries (SEI) two problems are evident:

- (1) For the type IIa diamond the quoted low frequency permittivity of 5.5 is less than the square of the reported refractive index  $(2.4)^2 = 5.76$ .
- (2) For the CVD diamond coating, the corresponding permittivity is given as 7.5 to 9.1 and the resistivity as being in the range  $10^7$  to  $10^8$  ohm cm.

It appears probable that problem (1) which is a clear violation of the Maxwell relations must be associated with the different sampling of the property in dielectric and refractivity measurement. Problem (2) is likely to be associated with

the incorporation of some residual graphitic carbon in the CVD films. It is perhaps interesting to note that in sol-gel derived silica films, residual carbon at the level of only some 500 ppm is enough to almost double the effective dielectric permittivity. In plasma assisted CVD films laid down onto siliceous substrates work at Penn State has shown clear evidence for the formation of a thin silicon carbide layer between the diamond film and the substrate. Tests have shown however that this ~200Å thick layer is not sufficiently conductive to form an equipotential under the film and thus that thin diamond films over silica substrates could be used in packaging. Further work will, however, be needed to improve the quality, flatness and speed of deposition to satisfy the needs in commercial application.

## GROWTH TECHNIQUES, THERMAL CONDUCTIVITY AND OTHER PROPERTIES OF CVD DIAMOND FILMS AND FIBERS

M. S. Dresselhaus

Since the summer of 1984, numerous Japanese visitors have passed through my laboratory, showing gorgeous diamond Raman spectra taken on diamond films. Because of the very high Raman cross section for  $sp^2$  bonded carbon relative to that for the  $sp^3$  bonding (a factor of  $10^2$ ), I was impressed that many Japanese were making real diamond films. In contrast, during that same time frame, American visitors were giving their attention to diamond-like films, perhaps motivated by their hardness, high electrical resistivity and compatibility with integrated circuits. The few American visitors who claimed to be making "diamond" films showed Raman spectra with a large  $sp^2$  signature. In this context, I was pleasantly surprised at the workshop to learn of the progress the Americans were making in synthesizing diamond films.

### Analogies Between Growth of CVD Diamond and CVD Graphite

The growth conditions for the CVD process for synthesizing diamond films are remarkably similar to these for CVD preparation of graphite films and fibers. In this context, let me review the basic steps in the growth of a carbon fiber by CVD to see whether any of this experience might provide insights for the CVD growth of diamond fibers. We start with small ( $\sim 100 \text{ \AA}$ ) iron particles for the catalyst which could be spread on a heated substrate ( $1100^\circ \text{C}$ ). As for the case of the diamond films, the temperature range over which the graphitic CVD growth occurs is very small! (perhaps  $1100 \pm 50^\circ \text{C}$ ). The carbon supply is provided by a hydrocarbon like  $\text{CH}_4$  (about 5% or less) in a  $\text{H}_2$  carrier gas -- again almost the same as for the diamond films, except that for the diamond case, the reaction takes place in a reactor containing a large concentration of atomic hydrogen.

Returning now to the synthesis of a graphite fiber by the CVD process, upon entering the reaction chamber the hydrocarbon is pyrolyzed and the residual carbon is absorbed by the catalyst particles. Upon saturation with the carbon, the catalyst particles spew out crystalline carbon in the form of a hollow fiber. The similarities of the two CVD processes suggest that perhaps diamond fibers can be made by a process similar to that for graphite fibers, except for the use of the plasma discharge to synthesize diamond fibers. This seems like a useful thing to try, and I would like to look into this myself in more detail.

To continue with the CVD method for preparing graphite fibers, the diameter of the fibers formed initially might be  $\sim 2000\text{\AA}$ . The second step in the fiber growth is a thickening process by CVD growth on the initial fiber substrate, reaching anywhere from  $5000\text{\AA}$  to more than  $100\mu\text{m}$  for the final fiber diameter. This CVD growth is carried out under similar though not identical conditions as for the initial fiber growth. The thickening process can be viewed as CVD epitaxial graphite growth on a graphite substrate. Finally, for realizing the highest degree of crystal perfection in a CVD graphite fiber, it is heat treated to  $\sim 3000^\circ\text{C}$  for a short time. I am not sure that a heat treatment process would be as satisfactory for the growth of an ordered diamond structure in a diamond fiber.

One neat thing that has been done recently is the CVD growth of graphite on a continuous commercial carbon fiber substrate. The advantage of this from an applications point of view is the following. CVD fibers cannot be made as continuous fibers. But the commercial fibers based on ex-polymer precursors which are made as continuous fibers do not have good graphitic ordering. By this CVD growth process, the advantages of both kinds of fibers can be achieved simultaneously: a core ( $\sim 10\mu\text{m}$  diameter) of a polymer based fiber, and a CVD sheath ( $\sim 100\mu\text{m}$  diameter) of highly graphitic material, all in a continuous roll. The analog of such a structure for

CVD diamond would be the preparation of a continuous fiber roll with a diamond sheath on the outside.

#### Increased Growth Rates

One of the objectives of the diamond film growth research is to find ways to increase the growth rate. In this context, let me briefly review the history of the CVD growth of carbon fibers and how rapid growth rates were achieved. There was knowledge about the CVD process for carbon fibers for many years (perhaps 50). Much basic research was done on the growth mechanism of carbon filaments during the 1960's. This fiber growth was considered a nuisance for surfaces exposed to carbon, because dust specks could nucleate the growth of sooty fuzz. In an isolated place in the mountains of Japan, Koyama and Endo developed a process with enough reliability, control, reproducibility and throughput, that it became of commercial significance. They took a number of steps which cumulatively led to high growth rates, including: cleanliness, control of catalytic particle size to be uniform and small (100Å), and use of a clean mullite substrate. Starting from a process with potential for commercialization, an order of magnitude or more further increase in throughput was achieved by (1) computer control, (2) use of suspensions of catalyst particles, and (3) use of solutions (e.g. ferrocene) to form catalyst particles upon thermal decomposition. More recently at least another order of magnitude increase in throughput was realized by the use of intersecting jets of ferrocene ( a catalytic precursor) and of hydrocarbon/ $H_2$  in the hot zone on a reactor, leading to a continuous high yield production process. Growth rates of ~1 mm/min have been realized with high fiber density growth. On the other hand, the crystalline perfection of the fibers grown by the continuous jet production process is not as high as that for the less efficient substrate methods. Perhaps intersecting jets of ferrocene and hydrocarbon/ $H_2$  in the hot zone of a plasma discharge reactor might generate diamond whiskers!

### Non-Planar Carbon Compounds

Under ambient conditions the stable form of carbon is graphite, composed of an AB stacking of honeycomb carbon (graphene) layers. The introduction of guest species into graphite is normally by intercalation, forming an ordered sequence of planar graphene and intercalate layers in a metallic intercalation compound where the layers are held together by ionic bonding forces.

Exceptions to this pattern are the insulating covalent compounds formed with fluorine and oxygen, where the carbon atoms are arranged on puckered layers as shown in the figure for  $(CF)_n$  and  $(C_2F)_n$

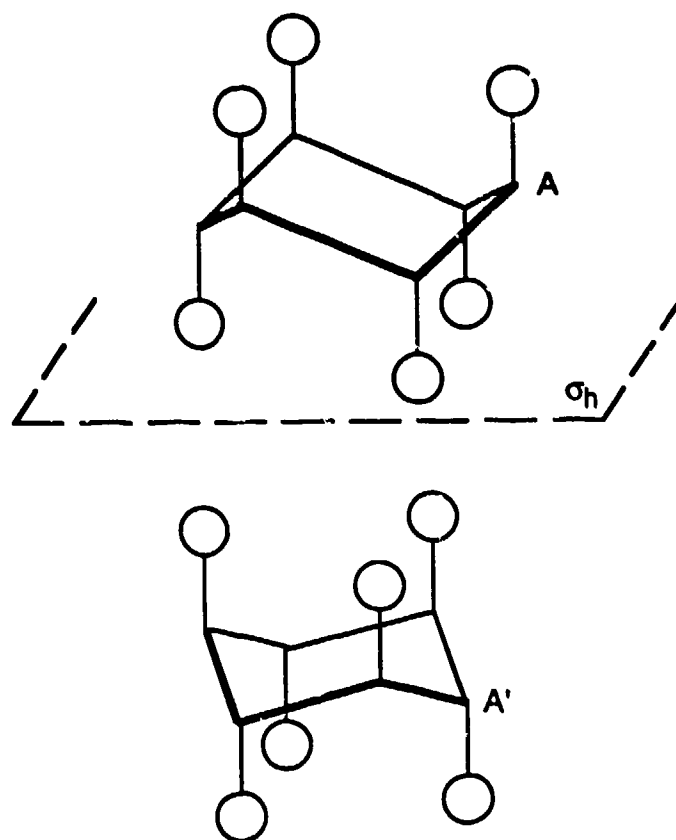


Figure 1.

This puckering concept can perhaps be exploited in preparing diamond films. For epitaxial growth of a diamond film, it may be possible to use fluorine as a catalyst to produce puckering on the surface carbon monolayer, and then to replace the chemisorbed F with carbon in the presence of atomic hydrogen. In the subsequent growth of the diamond film, it may be possible to use F to produce puckering on each newly deposited carbon layer and then to employ atomic hydrogen to remove the fluorine in the form of HF, using the same hydrocarbon feedstock as is now used for the growth without the fluorine, this concept might lead to faster growth rates and/or lower growth temperatures.

### Thermal Conductivity

Heat sinks for integrated circuits promise to be one of the major applications of thin diamond layers. This application is related to the fact that single crystal diamond possesses the highest thermal conductivity of any known material:  $K_{\max} = 1.2 \times 10^4 \text{ W/m}^2\text{K}$  at 70K for the best diamond ever reported. For this best diamond sample, K at room temperature is 2300 W/m<sup>2</sup>K. The room temperature value of 1300 W/m<sup>2</sup>K reported for the Sumitomo synthetic diamonds compares very favorably with that for good gem stones.

In considering room temperature operation, the thermal conductivity in the plane for the best highly oriented pyrolytic graphite (HOPG) is ~2500 W/m<sup>2</sup>K, is comparable to or slightly higher than that for diamond, and is much higher than that for copper (~500 W/m<sup>2</sup>K), as shown in the figure. Since the most highly ordered graphite fibers (prepared by CVD and heat treated above 3000°C) have room temperature thermal conductivities comparable to that for HOPG, graphite fibers have also been discussed for heat sink applications for integrated circuits.

The presence of the <sup>13</sup>C isotope in natural diamond gives rise to point defects and limits  $K_{\max}$  significantly. It is believed that the difference between the

highest possible  $K_{\max}$  (12,000 W/m<sup>2</sup>K) and the usual  $K_{\max}$  for gem stones (~3500 W/m<sup>2</sup>K) at 70°K is due to point defect scattering associated with the isotope effect. For example at  $T \sim 70\text{K}$  where  $K_{\max}$  occurs for the best diamond sample, the mean free path  $L$  calculated from  $K = C_p v L/3$  is as large as 1.3mm using  $v = 1.75 \times 10^4 \text{m/sec}$  and  $\rho_m = 3.51 \text{gr/cm}^3$ . On the other hand, at room temperature,  $L \sim 3\mu\text{m}$ , so that for 300K and above the isotope effect is unimportant.

Another topic of significance for the use of diamond films for heat sink applications is boundary scattering. Boundary scattering is important only when the diamond film dimension is less than the mean free path for the bulk sample (which is  $\sim 3\mu\text{m}$  at 300K). For a  $1\mu\text{m}$  diamond film of excellent crystalline quality, boundary scattering becomes of minor importance above  $\sim 300\text{K}$ , as shown in the figure below, where estimates for  $K(T)$  for a  $10\mu\text{m}$  thick diamond film are plotted with other relevant thermal conductivity data. We further note that for a  $10\mu\text{m}$  thick diamond film, the isotope effect is unimportant at room temperature and above, so no effort need be given to removing the small  $^{13}\text{C}$  fraction from the dominant  $^{12}\text{C}$  species.

It is quite remarkable that the thermal conductivities of diamond and graphite (in-plane) are almost identical and much higher than that for any other material. In both cases, the thermal conductivity is dominated by phonon contributions, which is surprising since graphite is quite a good electrical conductor and diamond is an excellent insulator. The explanation for the negligible electronic contribution of graphite is of course that, despite the high electrical conductivity, the carrier density is low ( $\sim 10^{-4}$ ) electron atom. Whereas, diamond has an intrinsically high thermal conductivity  $K$ , which is desirable for many applications, the presence of impurities, defects, crystal boundaries etc, could significantly decrease  $K$ , since  $K$  is proportional to the mean free path. For example, in disordered carbon fibers, a decrease in  $K$  by more than 2 orders of magnitude is observed relative to the ideal value. On the other

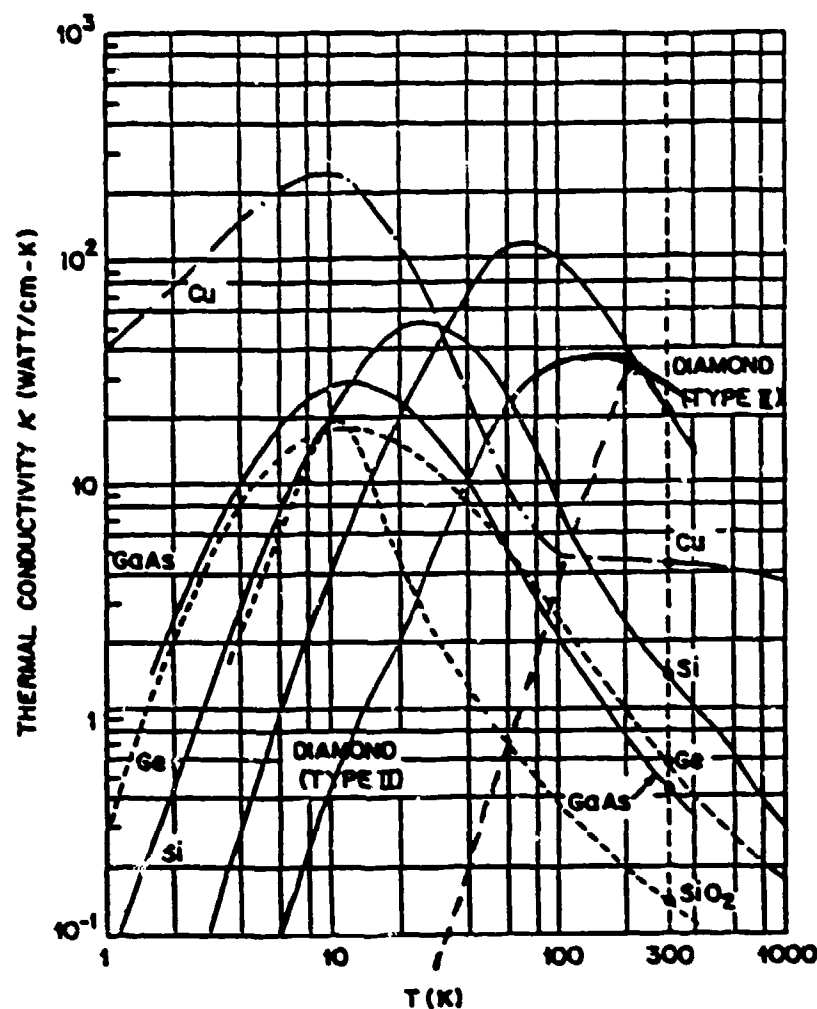


Figure 2.

hand, since diamond is a cubic material and graphite has a large anisotropy in  $K$ , the disorder-induced decrease in  $K$  for diamond should be very much less. On the other hand, if the processing steps needed to make a smooth thin diamond film introduce sufficient disorder to reduce  $K$  by an order of magnitude, then diamond films for substrates do not look so attractive. For example, the Lincoln etching process for thin film preparation involves prior ion implantation which introduces considerable lattice damage. The effect of such lattice damage on the thermal conductivity needs to be investigated.

## Cost

I do not see the cost of diamond as a significant issue. Using a figure of \$10,000/g, the cost of a heat sink ( $10\mu\text{m} \times 1\text{mm} \times 1\text{mm}$ ) would come to \$.35. Clearly the cost will be dominated by processing costs, like everything else in the semiconductor electronics business.

## POSSIBLE APPLICATION OF SYNTHETIC DIAMOND COATINGS IN SONARS

T. C. McGill

Recently the Sumitomo Electric has started to use synthetic diamond films to enhance the performance of speaker cones. Diamond's exceedingly high bulk modulus makes it ideal for the fabrication of acoustic devices (see Fig. 1). Sumitomo Electric is reporting improved response for speaker diaphragms using CVD coatings of diamond (see Figs. 2-4).

Given the success of the Japanese in the use of diamond films for this application, it seems desirable to examine the application of these films in acoustic sources and detectors for application in sonars. The unique acoustic properties plus the likelihood that it is very corrosion resistant to sea water may make it the ideal material for application in these important undersea applications.

### Suggestions

Hence, I would suggest an examination of the sonar receivers and transmitters with the objective of determining whether or not diamond thin films could provide major system improvement.

## DIAMOND COATED SPEAKER DIAPHRAGM

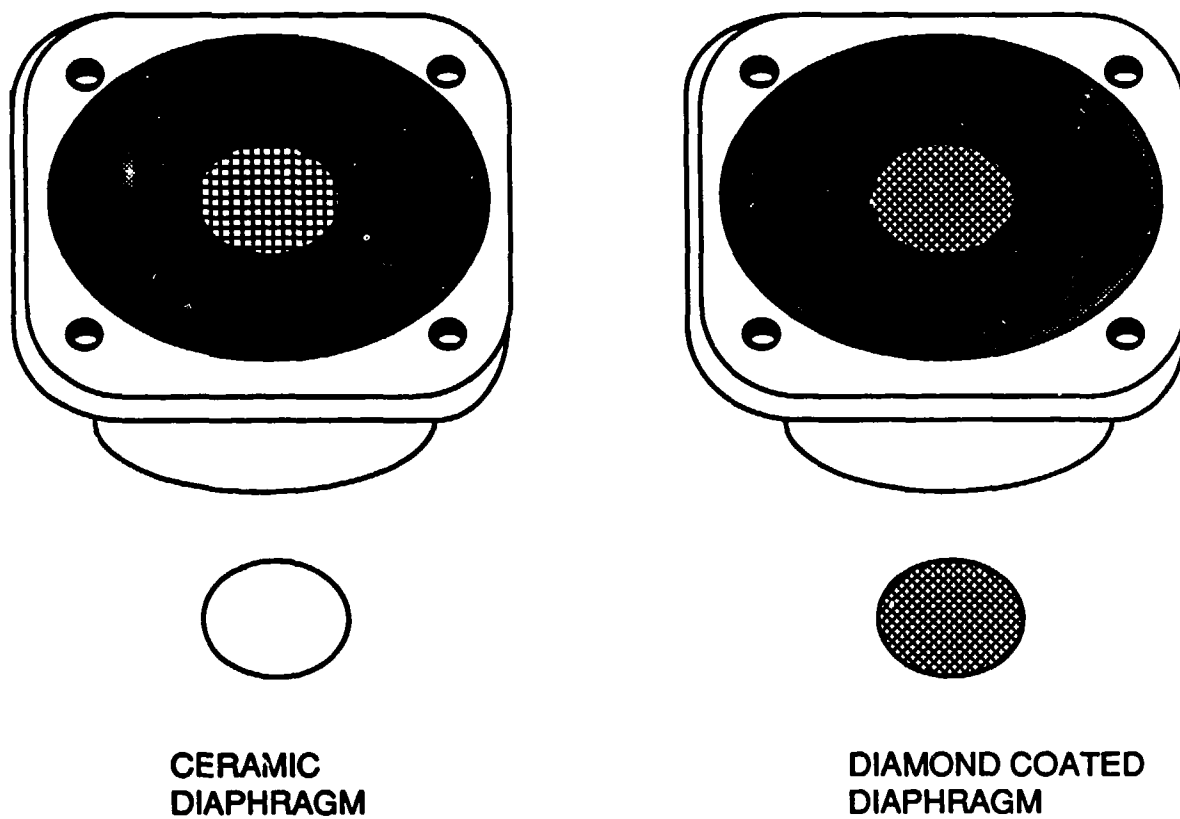


Figure 1. Picture of diamond coated diaphragm with a ceramic coated diaphragm. This figure was taken from the presentation made by T. Nakahara of Sumitomo Electric Industries, Ltd., to the Materials Research Council in July, 1987.

ACOUSTIC PROPERTY OF MATERIALS FOR DIAPHRAGM

MATERIAL	PARER	PLYLOPIREN	Al	Ti	Mg	Be	B	Al <sub>2</sub> O <sub>3</sub>	DIAMOND
SONIC [km/S]	1~2.4	1.3	5.1	4.9	5.1	12.2	13.5	11.6	18.2
YOUNG'S MODULUS [Pa]	4x10 <sup>9</sup>	1.5x10 <sup>9</sup>	7x10 <sup>10</sup>	1.1x10 <sup>11</sup>	4.4x10 <sup>10</sup>	2.7x10 <sup>11</sup>	4.2x10 <sup>11</sup>	5.2x10 <sup>11</sup>	1.2x10 <sup>12</sup>
DENSITY [g/cm <sup>3</sup> ]	0.2~0.7	0.9	2.7	4.5	1.7	1.8	2.3	4	3.5

Figure 2. The acoustic properties of materials for diaphragms. This figure was taken from the presentation made by T. Nakahara of Sumitomo Electric Industries, Ltd., to the Materials Research Council in July, 1987.

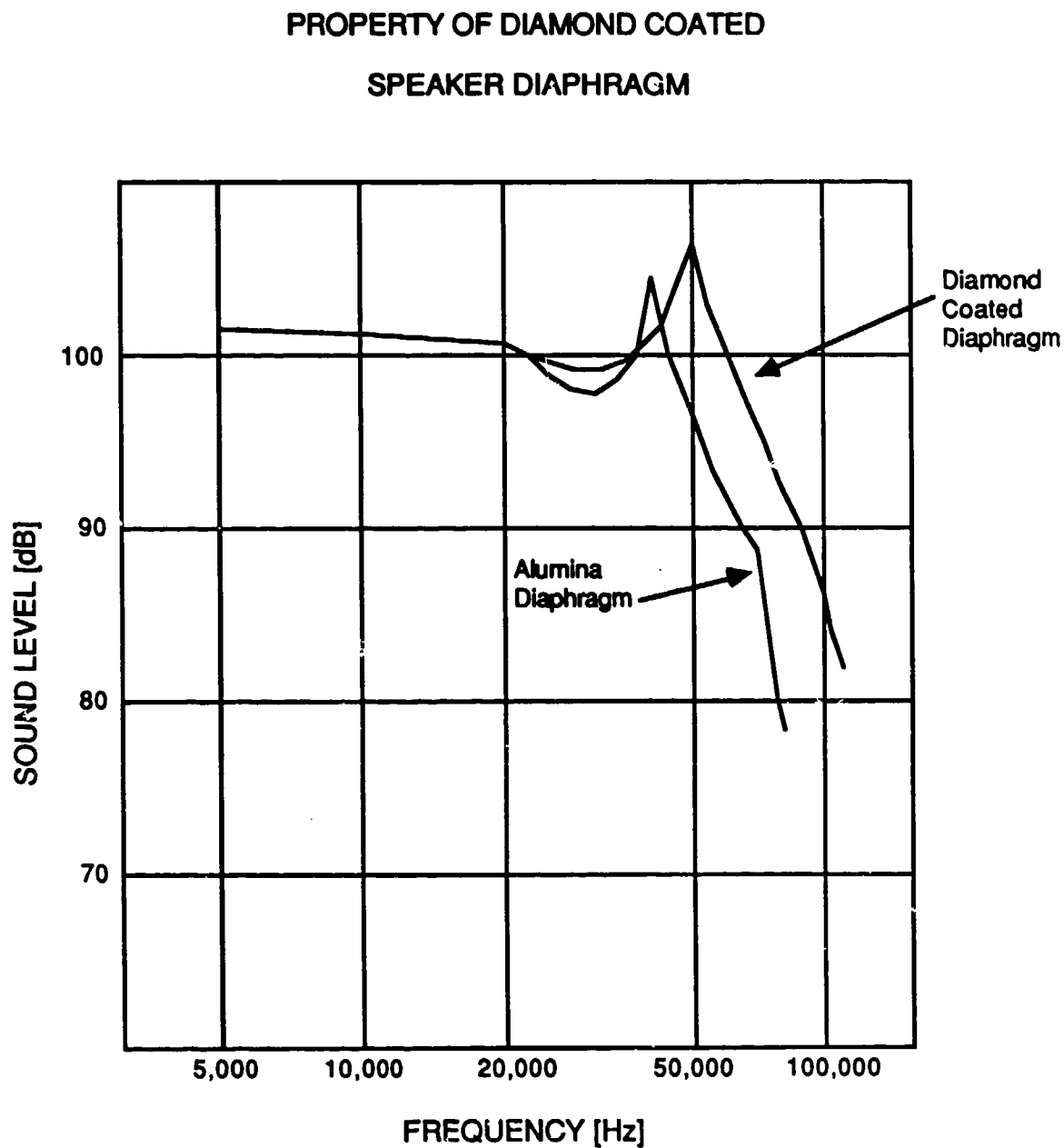


Figure 3. Comparison of diamond coated diaphragm with alumina coated diaphragm. This figure was taken from the presentation made by T. Nakahara of Sumitomo Electric Industries, Ltd., to the Materials Research Council in July, 1987.

# PROPERTY OF AMORPHOUS DIAMOND COATED SPEAKER DIAPHRAGM

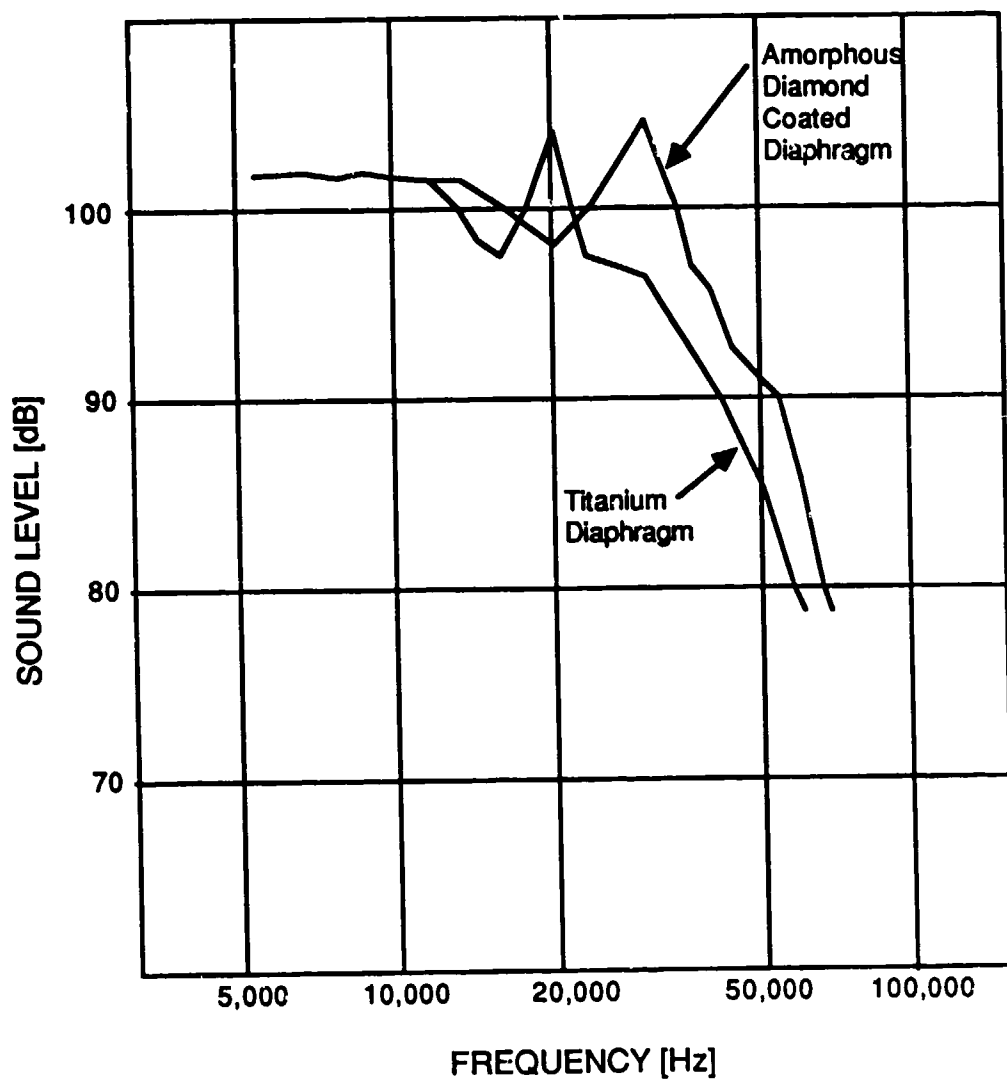


Figure 4. Comparison of diamond coated diaphragm with titanium diaphragm. This figure was taken from the presentation made by T. Nakahara of Sumitomo Electric Industries, Ltd., to the Materials Research Council in July, 1987.

## DISCRETE ELECTRONIC DEVICES OF DIAMOND

R. M. Osgood

The results presented by M. Geiss on diamond devices and diamond micro-fabrication indicate that the fabrication of making discrete diamond devices might be expected in the near future. These devices could work at very high temperatures due to the large diamond bandgap and at high power due to the high breakdown and high thermal conductivity of diamond. Discrete power transistors and diodes would be important for many DOD and civilian applications. This work on improved discrete components could have a major impact on lighter or more reliable power supplies. The potential attractive features of diamond-based discrete devices can be illustrated by considering the power-frequency product of an IMPA  $\pi$  microwave diode. This device is an important higher power, high frequency source, which incidentally is typically mounted on a diamond heat sink. In this case the product is proportional to the product squared of the breakdown electric field times the saturation velocity. In the case of diamond both of these quantities appear to be relatively large and as a result the power-frequency product is  $\sim 20$  times that of the same device made in silicon. Diamond devices appear to be extremely important for other classes of power devices. These devices or class of devices are listed in Table A.

TABLE A

DOD DEVICE APPLICATIONS FOR DIAMONDS

- HIGH POWER MICROWAVE  
DEVICES  
( 100 watts @ 100 Ghz)
- COMPACT HIGH POWER  
TRANSISTORS
- HIGH TEMPERATURE  
ELECTRONICS FOR HOSTILE ENVIRONMENT

### Doping of Diamonds

At present the fundamental impediment to the development of diamond electronic devices is the lack of ability to dope the material. There are three basic problems in doping diamonds: 1) Unacceptably high ionization energies for impurities; 2) Incorporation of n-type dopants, and; 3) Annealing of the material after implantation. While each of these problems is being studied currently, major difficulties exist in each area.

In the first area, silicon, GaAs and Ge have relatively high dielectric constants, i.e.,  $\epsilon > 10$ . As a result, the impurity ionization energies, which vary as  $\sim 1/\epsilon^2$ , are less than 0.1 eV, and the impurities are fully ionized at room temperature. The dielectric constant for diamond, is  $\sim 5.7$ , and thus one might anticipate that the ionization energies of 0.2 ~ 0.3 eV. This energy range is sufficiently high that the impurities will not be fully ionized at room temperature and the diamonds device would have to be heated to operate in a stable region.

Unfortunately the actual situation is somewhat less clear than this simple picture. At present there is some evidence that for the case of the best studied dopant, boron, that the ionization energy depends on the method of doping. Sumitomo has reported ionization energies of  $\sim 0.02$  eV for plasma CVD growth, while a corresponding number of  $\sim 0.2^*$  eV is accepted for ion-implanted samples. A further unknown is the type and number of alternate dopant elements, which can be used. At present it is unclear whether other acceptor impurities exist, which may have energies in the range of  $\leq 1$  eV.

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\* The measurement of this value seems to be at best questionable.

The second major difficulty is to find a suitable donor dopant. At present, only Sumitomo appears to have been able to incorporate donors (phosphorous atoms) in the diamond lattice. Their success was due to the use of doped CVD. However, while this approach worked extremely well for the case of boron doping (p type), only very low impurity concentrations were obtained ( $\sim 2 \times 10^{15}/\text{cm}^3$ ) in the case of n-type material. Other atoms such as Li may offer more hope; in fact a Soviet group has reported limited and irreproducible success in this area.

Finally, although successful doping has been realized by use of epitaxial growth (Sumitomo), a far more versatile way to incorporate impurity atoms is by means of ion implantation. In diamond, it is easy to implant, as in other electronics materials, but the necessary annealing step to regrow the diamond has not yet been accomplished successfully. The primary work on ion implantation in diamond in this country has been done by Geiss at Lincoln Lab. He has reported rapid annealing using an excimer laser but the details and reproducibility of this process have not been established. Other more conventional approaches to annealing have been unsuccessful because of the combination of high annealing temperatures  $\geq 2000^\circ\text{C}$ , and the relatively low temperature for carbonization  $\sim 500^\circ\text{C}$  of the diamond crystals.

## KINETICS/MECHANISMS FOR GROWING CVD DIAMOND

J. Stille

Although a number of different mechanisms have been proposed for CVD diamond formation<sup>1</sup>, there is too little experimental data available on which a rational mechanism can be founded.

Typically CVD diamond or diamond-like-films are prepared from methane/hydrogen mixtures (0.2-5.0% CH<sub>4</sub> in H<sub>2</sub>) at temperatures of 500-1000°C, but a variety of other organic reactants have been utilized, including low molecular weight alcohols, ethers and esters. The reaction can be carried out with a hot filament, in a plasma (microwave, Rf), or by assisted (UV irradiation, electron beam) CVD. In a number of cases, correlations have been made with crystalline diamond structure or deposition rate and such operating conditions as methane concentrations, total and partial pressures, temperature, flow rates, substrate material, substrate surface treatment, power, time etc.

These studies have provided the parameters that lead to optimal properties and growth rates, but have not provided any understanding of the reaction process. In order to arrive at a process that will give a high deposition rate and control of the structure of the material deposited, yet proceed at a relatively low temperature and yield a smooth surface, an understanding of the kinetics and mechanism of the reactions is necessary.

First, little is known concerning the identity of the reactive intermediates in the vapor phase. There are a variety of spectroscopic techniques that can be utilized (e.g., optical emission spectroscopy, mass spectroscopy) to identify such intermediates as methyl radical, methylene (carbene, singlet or triplet), and methyne. The spectra of these molecules are known and well defined. In addition, these species can be identified by

trapping just down stream from the substrate. Further, the presence of atomic hydrogen in the vapor phase needs to be verified.

Second, the relative concentrations of these reactive intermediates must be determined, so that the kinetics for the reactions can be established. Although the most prevalent species in the vapor may not be that which is responsible for diamond growth, by varying the reaction parameters, observing the concentrations of the intermediates and the growth rate, a better understanding of the process of attachment of a new carbon to a specific diamond surface - e.g., (111) plane - can be determined.

In addition, there are a number of relatively clean chemical methods of generating these different intermediates in the gas phase. For example, diazomethane is a source of carbene, uncontaminated with methyl radical or methyne. The generation of diamond or diamond-like materials from diazomethane-hydrogen mixtures should be carried out. The most energetic step in any mechanism involving methane is the initial breaking of a carbon-hydrogen bond (~100 Kcal/mole). Subsequent steps are less energy demanding. Carbene is known to rapidly insert into carbon-hydrogen bonds. Thus a deposition with diazomethane could take place at much lower temperatures, possibly minimizing graphite formation.

Mechanisms have been postulated in which acetylene is a key reaction intermediate, yet acetylene doesn't appear to have been tried as a reactant. A systematic survey of other reactants needs to be carried out.

Finally, the character of the diamond surface during or immediately after deposition needs to be examined by the many analytical techniques available. Detecting the presence of 3° hydrogen, 2° hydrogen, methyl groups and unsaturation ( $sp^2$ ) could greatly aid in understanding the mechanism of CVD diamond formation.

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1. See for example: M. Tsuda, M. Nakajima and S.O. Kawa, J. Am. Chem. Soc., **108**, 5180 (1986) and references therein.

## CVD GROWTH ON LEVITATED SINGLE-CRYSTAL DIAMOND OR c-BN

J. L. Margrave

Techniques for macro-scale growth of single-crystal diamonds from seeds usually require high pressures, high temperatures and long times. CVD growth on substrates usually yields amorphous or polycrystalline films and is very sensitive to the substrate temperature for the deposition. This note proposes a new technique for CVD diamond growth on cut slabs of natural/synthetic diamond or on small diamond or c-BN seeds.

Acoustic levitation is a well-developed technique for supporting small samples in heated gaseous atmospheres. Typically, the temperatures for acoustic levitation are 100-1000 K, just right for diamond CVD. A hot filament or moderate intensity Rf-discharge in  $\text{H}_2/\text{CH}_4/\text{B}_2\text{H}_6$  should provide an ample supply of  $\text{CH}_x\text{BH}_x$  (or whatever active species is needed).

Initial experiments to demonstrate the feasibility of acoustic levitation/heating of diamonds are being set up at Rice University. Adaptations to produce hybrid acoustic/electromagnetic (Rf or microwave) apparatus are also in progress. To deposit on low temperature substrates, laser-assisted CVD will be tried.

If one can acoustically levitate and heat small diamond or c-BN seeds, then macro-growth rates should be possible. In some cases, to avoid substrate problems, one might use small c-BN or diamond seed crystals in an acoustic levitation device with laser-assisted CVD. For B-doped diamond, it is proposed to use diamond seed crystals with an  $\text{H}_2/\text{B}_2\text{H}_6/\text{CH}_4$  Rf-plasma or a low molecular weight carborane or an alkyl borane.

This experiment could be especially appropriate for a space-processing experiment in which levitation would be free, low-pressure  $\text{CH}_4/\text{H}_2$  cheap, and

diamonds are the product. Even if large crystals cannot be grown, this could be an excellent technique for growing diamond or c-BN films on levitated substrates, i.e., carbide cutting/drilling tools.

## DENSE "DIAMONDLIKE" HYDROCARBON AND CARBON FILMS

J. C. Angus

Dense "diamondlike" hydrocarbon films are a new class of solid formed by a wide variety of plasma deposition and ion beam techniques. Their very unusual nature is shown in Figure 1, in which the atom number density is plotted versus the atom fraction hydrogen<sup>1</sup>. The atom number density,  $\rho_N$ , is defined by

$$\rho_N = \frac{\rho_M}{\sum x_i A_i} \quad (1)$$

where  $\rho_N$  is the mass density,  $x_i$  the atom fraction of element  $i$  and  $A_i$  the atomic mass of element  $i$ .

The "diamondlike" solids have number densities greater than any other hydrocarbon and fall between crystalline diamond and the adamantanes, which are hydrogen saturated molecular diamonds with 10 and 14 carbon atoms. Because the films are a dense, amorphous network of covalent bonds without apparent grain boundaries or pinholes, they have great potential for corrosion protection and as barrier layers for electronic and optical devices.

The mechanism of formation of the dense "diamondlike" films is not well understood. However, it appears clear that the presence of hydrogen and the average impact energy of the precursors on the surface of the growing film play important roles<sup>2</sup>. The diamondlike films are formed when ionized hydrocarbon fragments hit the surface with energies in the range from 50 to 200 eV. These conditions are easily obtained by direct low energy ion beam deposition from a Kaufman type ion source using  $\text{CH}_4/\text{Ar}$  or by rf self bias deposition. The latter technique is simply an rf sputter system run at lower voltages and higher pressures to reduce the average impact energy.

The mass and number densities of a series of dense "diamondlike" hydrocarbons prepared by F. Jansen<sup>3</sup> are shown in Figure 2. The mass density decreases with hydrogen content but the atom number density remains constant. Jansen and others have also measured the ratio of  $sp^3$  to  $sp^2$  bonded carbon in the films. These data can be interpreted using recent theories of random, covalent networks<sup>4,5</sup>. These theories indicate that the optimal average coordination number,  $m$ , should be  $\sqrt{6} \approx 2.45$ . Amorphous solids with average coordination number of 4 are highly over-constrained. (For the present purposes  $m$  is defined by

$$m \equiv 4x_3 + 3x_2 + x_1 \quad (2)$$

where  $x_3$  is the atom fraction of  $sp^3$  carbon,  $x_2$  the atom fraction of  $sp^2$  carbon and  $x_1$  the atom fraction of hydrogen.) The average coordination number is shown in Figure 3 as a function of atom fraction hydrogen. The measured values are in the range predicted by theory. Furthermore, the measured  $sp^3/sp^2$  ratio and the predicted ratio for  $m = 2.45$  are shown in Figure 4. Again reasonable agreement is observed.

It is clear from Figure 4 that the films become more "diamondlike", i.e., are increasingly dominated by  $sp^3$  bonding as the hydrogen content increases. This is because the low coordination number of hydrogen (one) permits a larger fraction of  $sp^3$  bonding (coordination number of four) while maintaining an average value near the optimal point.

Comparison of the dense "diamondlike" hydrocarbons ( $a-C:H$ ) with amorphous hydrogenated silicon ( $a-Si:H$ ) is of interest. Silicon differs from carbon in that it does not lower its average coordination number by formation of  $sp^2$  or  $sp^1$  bonding. The lattice strain in amorphous silicon is therefore more likely to be reduced by clustering than in the amorphous hydrocarbons. However, clustering into small graphitic "islands" may

occur in a-C:H and may allow the average coordination number to be somewhat greater than the optimal value predicted for a completely random network.

The properties of the dense "diamondlike" hydrocarbons are extreme. For example, Figure 5 shows the hardness of a series of diamond-cubic and zinc-blende solids versus atom number density. Despite the uncertainties in the measurements, it is clear that the dense hydrocarbons are unusually hard. Furthermore, preliminary measurements indicate the films are extremely impermeable. Apparent average diffusion coefficients for Ar are less than  $10^{-18}$  cm<sup>2</sup>/sec at 25°C compared with values in the range of  $10^{-6}$  to  $10^{-9}$  cm<sup>2</sup>/sec for diffusion of Ar in conventional hydrocarbon polymers<sup>6</sup>.

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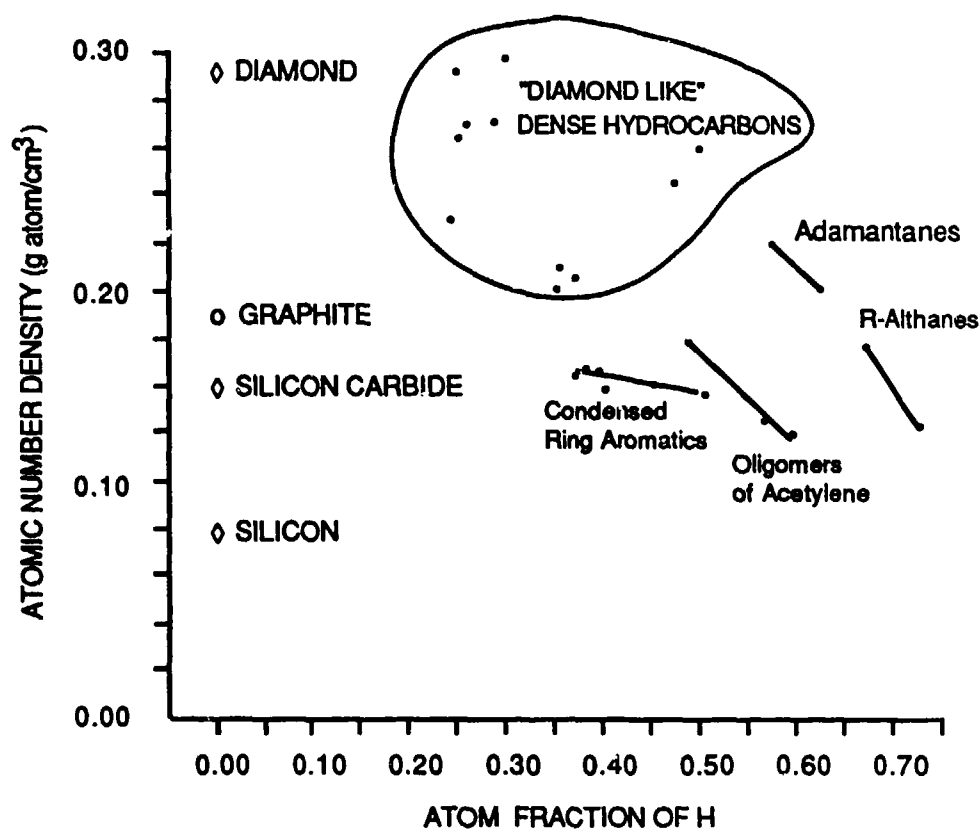
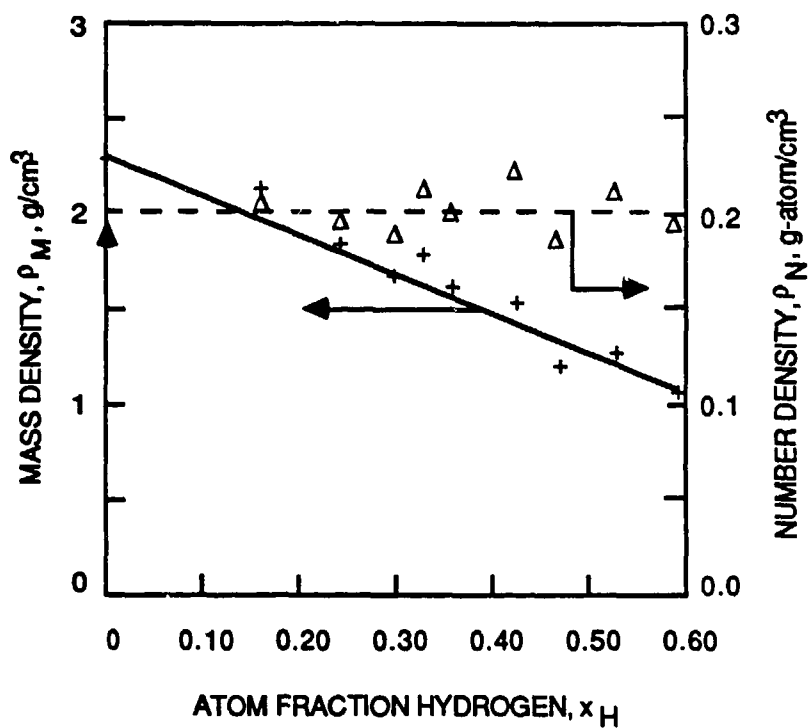


Figure 1. Atom Number Density versus Atom Fraction Hydrogen for a Series of Hydrocarbons.



RECALCULATED FROM DATA OF F. JANSEN

Figure 2. Mass and Number Densities of a Series of Dense "Diamondlike" Hydrocarbons Prepared by F. Jansen<sup>3</sup>.

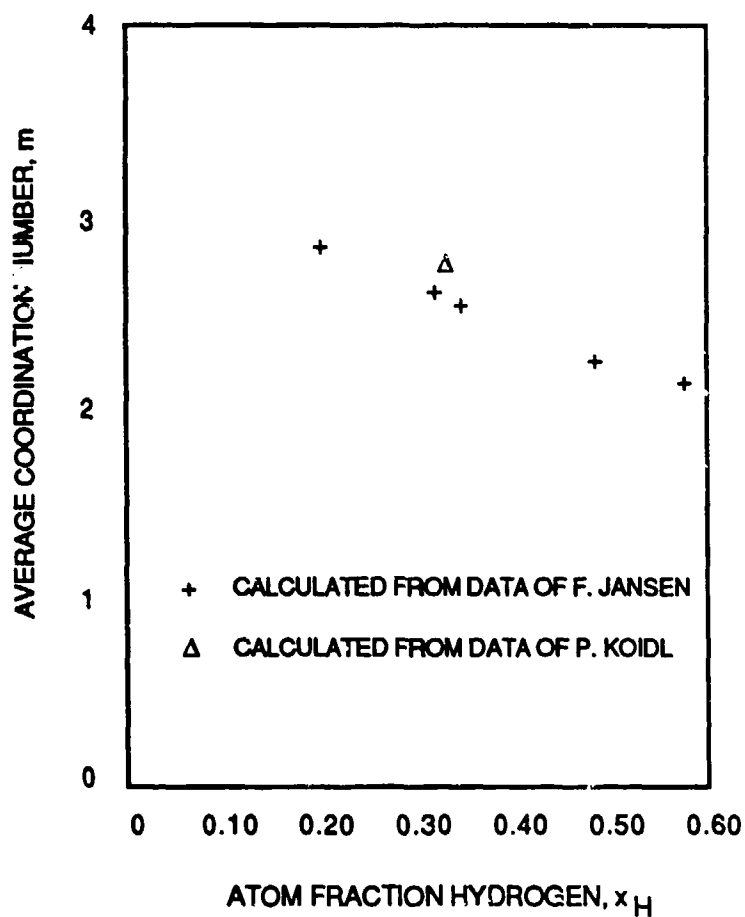


Figure 3. Average Coordination Number,  $m$ , of Dense "Diamondlike" Hydrocarbons versus Atom Fraction Hydrogen.

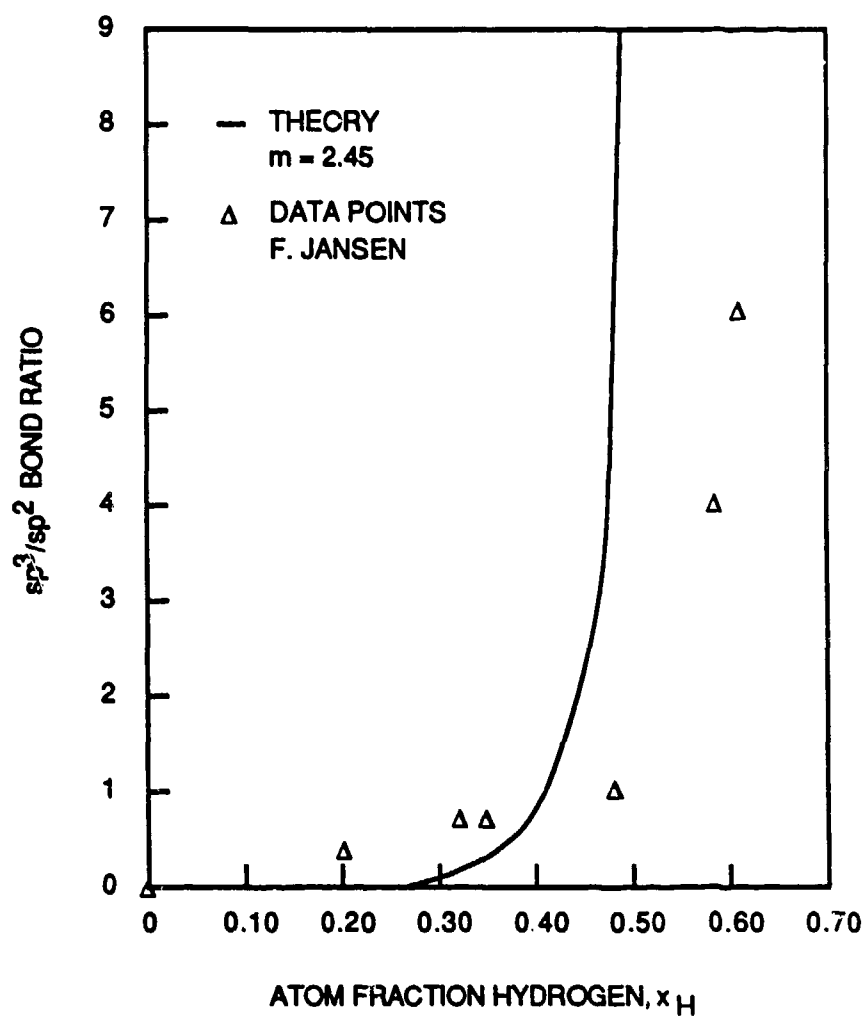


Figure 4.  $sp^3/sp^2$  Ratio versus Atom Fraction Hydrogen for Dense "Diamondlike" Hydrocarbons.

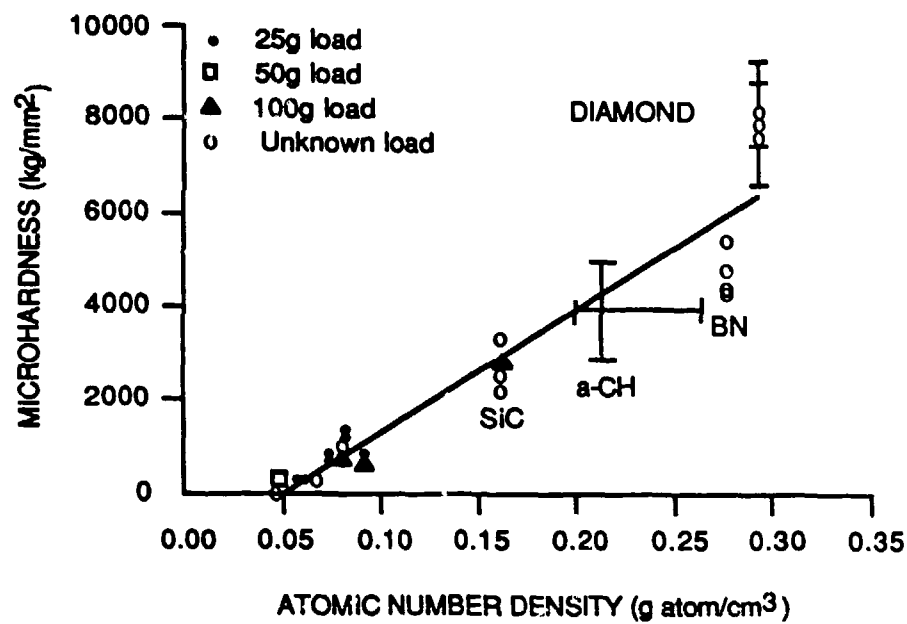


Figure 5. Hardness versus Atom Number Density for Diamond Cubic and Zinc Blende Solids.

## AGENDA

### MEETING ON ELECTROMAGNETIC SIMULATIONS, PACKAGING AND MEASUREMENTS ON HIGH-SPEED DEVICES

July 13-15, 1987

#### Monday, July 13, 1987

Introduction - S. Roosild (DARPA)

Introductory Remarks - B. Gilbert (Mayo/MRC)

#### I. SOLUTIONS TO MAXWELL'S EQUATIONS AT HIGH-FREQUENCIES

Method of Moments Applied to 2D and 3D Transmission Line Structures R. Harrington (Syracuse Univ.)

2D and 3D Electromagnetic Models at Frequencies Above 5 Ghz - T. Itoh (Univ. Texas)

Perspectives on Solutions to EM Problems - A. A. Oliner (Brooklyn Poly)

DISCUSSION

#### Tuesday, July 14, 1987

#### II. ISSUES IN PACKAGING FOR HIGH-SPEED DEVICES

VHSIC Packaging Strategies - Barry Whalen (MCC)

Novel 3D Packaging Concepts - Lionel Levinson (GE Corp. Res.)

Fine Line Connections - Peter Young (Boeing Microelectronics Res. Center)

Novel Ceramic Packaging Materials - E. Cross (PSU/MRC)

Perspectives on Materials for Packaging - R. Turney (IBM)

DISCUSSION

#### Wednesday, July 15, 1987

#### III. HIGH-SPEED CIRCUITS AND MEASUREMENTS

Conventional Measurements of High-Speed Devices - R. Dingle (Gain Electronics)

Measurements of High-Speed Devices with Superconductor Devices - Sudep M. Faris (Hypres, Inc.)

Optical Measurements of High-Speed Devices - D. Bloom (Stanford)

DISCUSSION

**ATTENDEES**  
**HIGH-SPEED PACKAGING**

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# **ELECTROMAGNETIC MODELING, HIGH FREQUENCY PACKAGING, AND PICOSECOND MEASUREMENTS**

**B. K. Gilbert, T. C. McGill, D. K. Ferry, R. M. Osgood, L. E. Cross  
and M. S. Drösselhaus**

## **INTRODUCTION**

During the past five years, considerable progress has been made in the speed, or "clock rate", at which silicon and Gallium Arsenide digital integrated circuits can operate. Logic gate delays of as little as 50-100 psec are making it possible to design mainframe computers and military signal processors which, during the next few years, will achieve clock rates of as great as 500 million clock ticks per second (500 MHz) and 2-5 billion clock ticks per second (2-5 GHz) respectively. Furthermore, Gallium Arsenide digital integrated circuits have already been demonstrated in the laboratory which perform useful functions at even higher clock rates, of up to 18-20 GHz. At these operating frequencies, digital computers are emitting and propagating electrical energy in that portion of the electromagnetic spectrum traditionally reserved for analog microwave communications channels and radar systems; these electromagnetic issues represent an unprecedented and totally new phenomenon for traditional digital systems designers, for which they are generally unprepared and unequipped. However, because these higher system clock rates can lead directly to computational rates up to one or two orders of magnitude greater than those at present, they will be pursued vigorously during the next decade.

Unfortunately, three supporting areas of the technology have not kept pace with the rapid increase in speed performance of the digital chip technologies. These areas are: 1) the inability to completely understand and quantify the complex electromagnetic events which occur as signals propagate along the metal interconnects between logic gates on the chips and between the chips on their circuit boards; 2) difficulties in the

fabrication of packaging and substrate structures which can simultaneously protect the chips and also provide high quality, wide frequency bandwidth signal interconnects between them; and 3) inadequacies in the ability to measure directly the performance of local regions of the functioning chips (referred to as "microprobing" of the chip), and limitations in the ability to measure the propagating electrical signals as they pass through the interconnecting medium between chips. Without progress in these areas, the designers of next generation signal processors will be unable to convert the advances in integrated circuit performance into enhancements in processor performance. All three problems are strongly interrelated; progress in any one of these areas might be delayed or rendered useless without parallel progress in the other areas.

Although it was apparent to the MRC membership that these problems must be solved in consort with one another, an equally strong perception developed that the research groups working in each of these three areas were unaware of the problems and partial successes in the other areas, and even for the need for the development of tools which would allow signal processor designers to operate in these high frequency operation regimes. Accordingly, a summer MRC workshop was held on July 13-15, 1987, to bring together the most capable and advanced workers in each of these three fields for the sharing of problems and results, and to assure interaction between the three groups. As predicted, the members of the different communities were not acquainted with one another's efforts, and a considerable amount of animated interaction took place.

The following paragraphs will first offer several suggestions for future research which are based on the outcome of the workshop, and thereafter will summarize briefly the presentations in the three specialty areas reviewed at this meeting.

## SUGGESTIONS

1. The solution of the modeling problems of high speed digital integrated circuits and circuit boards ("substrates") has received little attention to date, is one of the principal linchpins of the next generation of digital computers and signal processors, and is now within reach based on the virtual explosion of new mathematical modeling techniques over the past several years. A modest level of funding would be adequate to perform this urgently needed research task, particularly if the funding were employed to support a CONSORTIUM of the best minds in the country to attack these problems in a concerted and organized effort. However, it should be cautioned that such a consortium should be established with clear ties to the computer and signal processing communities, so that the real world problems of advanced computers can be continuously brought to the attention of the electromagnetics theoreticians.

2. All packaging development for next generation digital processors should concentrate on high interconnect density circuit boards, or "substrates", for multichip modules; these substrates must demonstrate excellent electrical characteristics and fine metal line patterning capabilities. It seems clear that interconnect densities must approach 1000 linear cm per square cm of real estate, at least for some important applications. In these regards, the techniques of: 1) overlaying conductors on top of integrated circuits; 2) of building up very high interconnect densities; and 3) of creating composite inorganic substrates with regions of low dielectric constant material, and other regions with high dielectric constant material, in combination with control of interconnect metalization in three dimensions; are particularly noteworthy. These developments would benefit to a considerable extent by encouraging collaborations between the researchers developing these new materials and methods and the commercial companies which manufacture packages and substrates for the U.S. electronics

community. Such a collaboration would assure that new materials developments are moved from the laboratory to the factory floor in a timely and expeditious manner.

3. Two classes of techniques for measurement of high speed electrical and optical events are particularly meritorious, and deserve support. The first of these is the method of measuring integrated circuit performance by transmitting laser light through the back of the integrated circuit or wafer and measuring the polarized light reflected from the back surfaces of the metal conductors. The second method which appears to justify support is the use of femtosecond pulses of laser light to characterize the device physics behavior of materials and devices into the 6 terahertz range. These two methods are very strongly complementary, and should both be supported to expand the range of frequencies over which the behavior of electrical and optical devices can be measured and characterized.

#### **SUMMARY OF THE PRESENTATIONS GIVEN AT THE MRC SUMMER WORKSHOP** **Electromagnetic Modeling of the Interconnect Environment**

Approximately a half dozen laboratories in the country are engaged in the development of new theoretical insights into the behavior of propagating electromagnetic wavefronts in complex three dimensional metal-dielectric structures such as microwave waveguides, computer printed circuit boards, and the metal interconnects on an integrated circuit. The initial theoretical underpinnings to this science were provided by Maxwell and others late in the last century and early in this century. Although an additional burst of research activity took place in the 1960's, the entire decade of the 1970's passed with little advance in this area. During the past five years, however, there has been a resurgence of activity, with the development of a dozen or more new theoretical approaches, which are just beginning to be explored; it is generally agreed that these new methods are still very far from being completely

explored. The speakers at the MRC conference presented a cornucopia of new approaches, including the method of moments, a method of images, spectral domain techniques, finite element and finite difference methods, field or mode matching techniques, and full wave solutions, all with strengths and weaknesses, but all much more general, powerful, and computationally efficient (in some cases by several orders of magnitude) than those available just a few years ago. Two generic classes of methods were discussed. The first class uses several simplifying assumptions (referred to as the "quasi-TEM assumptions") to derive sets of computationally efficient electromagnetic solutions for signals with frequency components from DC up to approximately 5 GHz). The second class, referred to as "full wave solutions", is much more difficult, is the subject of extensive research at present, and will eventually allow the analysis of complex electromagnetic interactions at frequencies beyond 5 GHz. Issues of signal radiation ("antenna effects") and dispersion can also be analyzed by these emerging methods.

The advent of supercomputers has greatly aided the ability to investigate the usefulness of these new methods, whose comparative strengths and weaknesses have yet to be completely understood or resolved. However, it is clear that they will be able to provide a much clearer understanding of sandwiches of metal conductors buried in dielectrics of much more complex two and three dimensional geometries (which are thus much more typical of actual computer interconnect structures) than heretofore possible. The methods promise to allow the modeling of the electromagnetic environment, and the propagation of short duration electrical pulses through actual fine-geometry conductors, in a much more accurate manner than heretofore. The ability to simulate accurately the propagation of high frequency pulses in lossy conductors, around corners, past discontinuities, and between different levels in a computer board, as well as the accurate

calculation of crosstalk between adjacent signal lines, appears to be within reach using the new techniques or their logical extensions.

It is noteworthy that none of the specialists in this field were even aware that a host of new problems has arisen in the digital field, and none of the presenters were working in this area; all of them have been concentrating on problems of monolithic microwave integrated circuits set for them by the microwave community more than a decade ago. This group of theoreticians expressed general surprise that their services were urgently required in a new field, and great enthusiasm for becoming involved in these new areas, which have constraints and problems quite different from those of the microwave world. The researchers themselves suggested that a consortium be formed to attack these problems in a concerted manner. The services of this small group of theoreticians is sorely needed to solve the electromagnetic environmental problems of the next generation of supercomputers and digital signal processors.

#### Advanced Materials and Methods for Packaging and Interconnect of Next Generation Computers

The second set of presentations reviewed the state of development of enhanced methods of packaging and interconnecting the next generations of high frequency digital and monolithic microwave integrated circuits. The speeds of the chips are becoming so great that the conventional method of encapsulating each chip in its own protective package, then mounting the packages on a circuit board, wastes too much space and hence causes excessive signal delays between the integrated circuits; the chips will have to be attached side by side (in a "brick wall" configuration) directly to an advanced circuit board, or "substrate", and then sealed against the environment as a single unit.

The advanced development work in this field is attempting to derive new methods for creating substrates which can support very dense interconnects (up to 1000 lineal cm of interconnect per square cm of substrate real estate), fine line geometries (down to 5

micrometers in width, and comparable to those on the integrated circuits themselves), and favorable electromagnetic properties (low waveform degradation and low crosstalk).

The discussions and presentations reviewed several new techniques for fabricating advanced substrates. In one approach presented, integrated circuits of the same or different families and/or technologies are placed in "brick wall" fashion directly on a substrate, which is used to distribute power and ground supplies to the chips; the substrate does not, however, support the signal interconnects. A thin mylar layer is overlaid ON TOP OF the chips, and a computer controlled laser or other photolithographic processes are used to pattern metal interconnect line directly onto this mylar overlay. Up to two levels of interconnects can be deposited on the mylar overlay. Connections (or "vias") to the underlying chips are made by burning a hole through the mylar to the chip contact pads, and then metallized to form the electrical connection. This general approach, while still very early in development, appears to have considerable promise for supporting very dense interconnects. The company which is developing this approach does, however, appear to have some reservations regarding its ability to support clock rates above 100 MHz; further modeling and testing will be required to resolve the maximum system clock rates and signal risetimes which can be supported by this particular packaging method.

A second technique described allows very fine copper interconnects to be laid down on a proprietary substrate material (probably polyimide on a silicon wafer substrate); the line geometries are 8 x 6 microns, with 8 to 16 micron spacing between parallel lines. To the present, the ability to lay down two layers of these dense interconnectors has been demonstrated. The geometric conformation of the lines, which can extend for many inches if required, is excellent, and individual breaks in the as-fabricated lines can be inspected and repaired using a proprietary process which was not described.

A third presentation, from one of the university research laboratories, described ongoing work to develop INORGANIC dielectric materials for electronic substrates with electrical and mechanical properties which may rival those of the more typically employed organic materials. To be able to control the propagation properties of the interconnects, the substrate designer must be able to place materials with very high relative dielectric constants (K values) in some regions of the substrate, and very low K values in other portions of the same substrate. The lowest K materials used to date have been Teflon ( $K = 2$ ) and polyimide ( $K = 3-3.5$ ). Teflon exhibits poor mechanical strength, leaving polyimide as the material of choice AT PRESENT. Inorganic materials exhibit K values from 5 to 11, a serious disadvantage based on the above comments. Recently, however, advanced inorganics research has led to the development of inorganics with K values as low as 1.8-2.2, along with the ability to photopattern very fine metalization geometries on these substrates, perhaps even with control of the resulting metal structures in three dimensions. The processes generally are carried out at low temperatures, allowing high conductivity metals to be employed. Several materials/methods were described, including sol-gel processes, macro defect cements, and sputter deposited columnar Silicon dioxide containing more than 50% void space hence the low K value, since the structure contains so much air).

A lengthy discussion was held regarding the potential value of the new Type II high temperature superconductors if employed as conductors on these substrates. The acknowledged problem in the interconnects of presently available electronic circuit boards and substrates is that as the cross sections of the conductors on these substrates decreases, the series resistive losses of the lines can increase to the point that much of the propagating signal is dissipated in the interconnect, robbing the computer or signal processor of its immunity to externally generated electrical noise or interference. There

was no question that methods need to be found to reduce the effective resistivity of the interconnect lines, and perhaps also of the power and ground supply busses.

However, the mixed views voiced at the workshop regarding the value of Type II superconductors in such cases reflects the uncertainty of the community of the conditions under which these new superconductors will become useful. For example, it was pointed out that the resistance of copper decreases by a factor of 7 at liquid Nitrogen temperatures, so that at 77 degrees Kelvin, the interconnect resistances may not pose an appreciable design problem. Thus, it was noted, Type II superconductors operating only at 77 degrees Kelvin may not have enough to offer except when signal propagation lengths are very long. However, as the transition temperatures of the superconductors increases toward room temperature, and provided that the critical current levels of the Type II materials can also be raised sufficiently, these materials may indeed eventually play a significant role in advanced interconnect technologies. Conversely, other participants at the MRC workshop argued strongly that superconductors could indeed play an important role even at 77 degrees Kelvin; a unanimous agreement was not achieved on this matter. For a further discussion of these issues, please refer to the Appendix at the end of this report.

Finally, several general comments regarding the entire discipline of advanced electronic packaging were made by two of the workshop participants representing the point of view of industry. It was pointed out, both by a representative of a large computer manufacturing company and by a senior staff member of the Microelectronics and Computer Consortium (MCC), that to be truly successful, ANY advanced packaging techniques must SIMULTANEOUSLY account for the following issues: interconnect densities, the delivery of "clean" power to the chips, adequate heat removal, excellent electrical properties, and excellent manufacturing yield at reasonable cost per substrate.

## New Techniques for the Measurement of Extremely Wideband Analog and Digital Signals

The third portion of the session reviewed advances in both the generation and the measurement of extremely short electrical pulses, as might be typical of a high clock rate digital signal processor or a microwave integrated circuit. Several techniques were presented. In one method, the performance of a Gallium Arsenide chip or substrate is probed from the back surface of the wafer, by propagating laser light through the wafer, and reflecting it from the under surfaces of the (optically reflective) metal conductors. In its round trip passage through the GaAs substrate, the relative phase of the laser light is altered by the electrical fields set up by the propagating signal wavefronts; these phase changes can be detected by comparison with a sample of the unaltered laser beam. This method, which samples different portions of a repeated signal to build up the entire signal waveform, should work well for pulses of up to 110 GHz bandwidth.

In another method, a small prism structure of Lithium Tantalate, of dimensions small enough to be used as a probe, is lowered onto a circuit board from its upper side, until the tip penetrates the electric field emanating from the signal traces or components. A laser beam passes along the long axis of the probe, and is completely reflected from facets ground into the tip end of the probe. The electric field to be measured creates a change in polarization of the laser light due to birefringence effects; again, this change in polarization can be detected and the results presented as a sampled, time varying waveform.

In yet another method, optical pulses as short as  $6 \times 10^{-15}$  seconds in duration are used to optically excite materials and structures of interest. The characteristics of the materials cause an amplitude modulation of these short optical pulses; optical rectification of the short pulses after they have emerged from the material or structure under test results in an ELECTRICAL pulse which is the ENVELOPE of the original

OPTICAL pulse which was used to probe the material or structure under test. In this manner, amplitude and frequency spectra can be measured from device physics events over a range from DC to approximately 6 terahertz ( $6 \times 10^{12}$  Hz).

In a final method described, pulses propagating down transmission lines were sampled using a pulse laser activated GaAs photoconductor activated by a pulsed laser; the photoconductor acts as a picosecond switch to sample energy from a propagating wavefront on a microwave transmission line.

One final presentation described the design and microfabrication of nonlinear transmission lines, by which a nonlinear shock wave effect is able to markedly shorten the falltimes (while lengthening the risetimes) of biphasic pulses. This technique, when perfected, should allow the generation of electrical pulses with falling edges of as little as 3-4 psec. These shock wave transmission line devices could then be used in the manufacture of Time Domain Reflectometry devices with much higher bandwidths than presently feasible (for many years and until very recently, the state of the art for TDR devices has remained constant at approximately 35 psec).

## APPENDIX

### ON THE POSSIBLE USE OF HIGH $T_C$ SUPERCONDUCTING MATERIALS

M. S. Dresselhaus

At the MRC summer workshop on electromagnetic modeling and substrates, the use of high  $T_C$  materials for high frequency applications and for power buss applications were discussed. The following paragraphs represent additional background material on these issues.

High  $T_C$  superconductors could well be important for high frequency applications. Because of our very limited knowledge of the high frequency properties of high  $T_C$  superconductors, we cannot yet make definitive predictions about the ultimate potential of these materials for such applications. We can nevertheless identify a number of attractive features of these materials for high frequency applications as well as a number of research and development issues that need to be addressed. The author of this section is personally involved with these issues at this time, because of prior background in the microwave properties of conventional superconductors.

Whereas the DC resistance of a superconductor vanishes below  $T_C$ , this is not the case at high frequencies, where superconductors are characterized by a complex surface impedance  $Z = R + iX$ . The high frequency regime is confined to frequencies  $\hbar\omega < E_g$ , where  $E_g$  is the superconducting bandgap. The functional form of the real part of the high frequency surface impedance (the surface resistance  $R$ ) for conventional superconductors is given by

$$R_s = R_{BCS} + R_{RES}$$

where the dominant BCS contribution is given by

$$R_{BCS} = r \omega^{\alpha} \exp(-\Delta / kT) / kT$$

In which  $R_{RES}$  is the residual (extrinsic) resistance and  $\Delta = E_g / 2$ . The most common superconductor in use for microwave cavity applications is the type II superconductor Nb, for which the zero temperature bandgap is  $E_g(0) = 2 \Delta = 3.7 k T_C$ , where  $T_C = 9.5$  °K, and the exponent  $\alpha = 1.63$  for the frequency dependent factor. Thus, as  $T$  falls below  $T_C$ , then  $R_S$  decreases by 2 orders of magnitude in a small temperature interval.

Though we do not yet know if this functional form for  $R_{BCS}$  is valid for high  $T_C$  superconductors, this formula can probably be used for estimation purposes, since its origin is strongly dependent on the existence of a superconducting band gap, and to a lesser degree on the specific mechanism responsible for superconductivity. By increasing  $T_C$  from 9.5 K for Nb to 95 K for  $YBa_2Cu_3O_7$ , the factor  $\exp(-\Delta / kT) / kT$  decreases by several decades, keeping  $T$  constant.

However, a major advantage for using high  $T_C$  superconductors is to exploit the superconductivity at temperatures of 77K and above. The following argument shows that 77K operation of a material with  $T_C \sim 95K$  is attractive. On cooling the  $YBa_2Cu_3O_7$  to 77K, we would expect the bandgap to reach 72% of its  $T = 0$  value. As materials with higher  $T_C$  are developed, higher operating temperatures may well become possible, or alternatively better performance at present operating temperatures can be realized. Reliable measurements of the temperature dependence of the surface impedance for high  $T_C$  superconductors are needed to place these arguments on a sound scientific foundation.

As electronics get faster, low loss propagation at increasingly high frequencies becomes of interest. Since superconducting behavior requires  $h \omega < E_g$ , the increase of the bandgap for high  $T_C$  materials by an order of magnitude (relative to the prototype conventional high frequency superconductor Nb) makes the high  $T_C$  materials attractive

candidates for very high frequency applications (especially in the frequency regime where  $\hbar \omega < E_g$  is not satisfied by Nb). From the functional form of  $R_{BCS}$  we see that for a given superconducting material, increasing  $\omega$  results in an increase in  $R_{BCS}$ . To evaluate the high frequency potential of the high  $T_C$  materials, study of the frequency dependence of the surface impedance is needed.

One major unknown issue regarding high  $T_C$  materials is the value of the residual surface resistance  $R_{RES}$ . For conventional superconductors  $R_{RES} \ll R_{BCS}$ . Preliminary studies on the surface resistance of high  $T_C$  materials suggest that compressed powders of the high  $T_C$  superconductors may have a high value of  $R_{RES}$ . This needs to be confirmed. It is likely that a significant amount of research will be needed to reduce  $R_{RES}$  to a range where the high  $T_C$  materials are useful for high frequency applications. When using high  $T_C$  materials as circuit components, it will also be important to match the impedance of the superconducting component to the rest of the microwave circuit; research and development work will also be needed to overcome this impedance matching problem.

At the summer MRC workshop, there was considerable discussion about Type I vs. Type II superconductors. In this regard, the high  $T_C$  superconductors differ from conventional Type II superconductors such as Nb in two ways; these two properties are actually closely related to each other for BCS superconductors. Firstly, for Nb the superconducting coherence distance  $\xi$  is comparable to the superconducting penetration depth  $\lambda$ , whereas for the high  $T_C$  materials  $\xi \ll \lambda$ ; we note that the condition  $\xi < \lambda$  distinguishes Type II superconductors from their Type I counterparts. Secondly, for Nb the lower critical field  $H_{C1}$  (below which there is no flux penetration) is close in value to the upper critical field  $H_{C2}$ , above which there is no flux exclusion, while for the high  $T_C$  materials,  $(H_{C2} / H_{C1})$  is believed to be huge (perhaps as large as  $10^4$ ). In the magnetic field region between  $H_{C1}$  and  $H_{C2}$ , there is finite flux penetration in terms of

flux vortices, which characterize the Type II materials. To this writer's knowledge, the implications of the condition  $\xi \ll \lambda$  on the high frequency surface impedance of the high  $T_C$  superconductors has not been studied in detail. Since most high frequency applications do not require external DC magnetic fields, and since typical high frequency magnetic fields are much smaller than  $H_{C1}$ , no flux penetration associated with the formation of flux vortices should occur under ideal circumstances (no trapped flux or edge effects). Studies of the behavior of the high frequency properties of high  $T_C$  materials in magnetic fields are also needed to assess the potential of these materials for use in the presence of magnetic fields. Since  $H_{C2}$  is so much larger than available magnetic fields, much of the emphasis should be devoted to an understanding of flux pinning phenomena in the large magnetic field range between  $H_{C1}$  ( $\sim 1$  k G) and  $H_{C2}$  ( $\sim 1$  MG).

As power density requirements for busses in integrated circuits continue to increase, the use of low loss superconducting power transmission elements might become attractive. With presently available superconducting materials, we must assume operation using liquid nitrogen as a refrigerant. At this temperature, the high  $T_C$  superconductors may not be worth the effort in comparison with copper, which exhibits a decrease in resistivity by a factor of more than 6 on cooling from 300 K to 77 K. High  $T_C$  superconductors may nevertheless be attractive for applications where size reduction of the busses is necessary, provided that the high current carrying capacity recently demonstrated in polycrystalline films can be achieved in the buss material. As  $T_C$  values continue to increase (hopefully up to 400 K), the high  $T_C$  materials become increasingly attractive for power buss applications. The option of using high  $T_C$  materials for power interconnects is of sufficient interest to merit continued materials research and development at this time.

**AGENDA**  
**HIGH TEMPERATURE COMPOSITES**

July 13-15, 1987

**Monday, July 13**

**TOUGHENED BRITTLE MATERIALS - Chairman: A. G. Evans**

**Ductile Phases**

Micromechanics - B. Budiansky (MRC)

Processing

Ceramic Matrices - I. Aksay

Intermetallic Matrices - R. Mehrabian

**Fibers/Whiskers**

Micromechanics - A. G. Evans

Processing - H. K. Bowen

**DUCTILE MATRIX MATERIALS - Chairman: J. C. Williams**

Micromechanics - G. Dvorak

Processing - R. Mehrabian

**INDUSTRIAL COMPOSITE MATERIALS - Chairman: J. C. Williams**

General Electric Materials - A. Johnson

Martin Marietta Materials - J. Venables

Lanxide Materials - A. Urquhart

Pratt & Whitney Materials - R. Anderson, A. Giamei, M. Blackburn

McDonnell Douglas Materials - S. Sastry

**Tuesday, July 14**

**INTERFACES IN COMPOSITES - Chairman: M. Ruhle**

Structure and Chemistry - M. Ruhle

Mechanics of Interface Cracks - J. Rice

Elastic/Plastic Analysis - F. Shih

Simulation of Interfaces - M. Eberhart

DISCUSSION

Relations Between Structure and Fracture Resistance - Discussion Leader: J. Rice

CREEP AND CREEP RUPTURE - Chairman: J. Hirth

Reinforcements - R. McMeeking

Creep Thresholds - A. G. Evans

DISCUSSION

Optimum Composite Microstructures - Discussion Leaders: J. Hirth, A. G. Evans

Wednesday, July 15

COMPOSITE PROCESSING - Chairman: R. Mehrabian

Thermodynamics - A. Chang

Kinetics of Solidification - J. Perepezko, W. Boettinger, R. Mehrabian

Colloidal Aspects - F. Lange

HIPing - R. McMeeking

DISCUSSION

Microstructural Evolution During Processing - Discussion Leader: R. Mehrabian

NEW FIBERS/WHISKERS AND COATINGS - Chairman: H. K. Bowen

Available Materials: A Survey - M. Rigdon

Coatings for Fibers - T. Gulden

Optimum Properties and New Ideas - P. Morgan

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## STRUCTURAL COMPOSITES

R. Mehrabian, A. G. Evans, J. C. Williams, M. S. Dresselhaus and P. Parrish

### INTRODUCTION

Structural metal and ceramic matrix composites have potential applications in military systems ranging from aerospace to armor to rapid-fire high projectile velocity gun barrels. A 30 to 40% potential improvement in thrust to weight ratio of advanced jet engines is predicted through the use of new high temperature composite materials. External structures of the new transatmospheric vehicle (NASP) require development of high temperature reinforced titanium intermetallics. Ceramic matrix composite bores, possibly in combination with metal or metal matrix composite jackets, have the potential to significantly improve the performance and durability of gun tubes by reducing erosion and distortion.

A new approach to the development of high performance composites has emerged through the initiatives of the DARPA/MRC. The central thrust is to exploit microstructure design principles based on micromechanics models to guide the material processing "pathways" for production of the composites. This approach (Fig. 1) forms the basis of a number of research and development programs, sponsored by DARPA and other DoD agencies, in industry and universities (i.e., through the University Research Initiative Program). This report of the MRC workshop follows the same sequence, starting with toughening and creep resistance concepts for composites that guide the design of optimum microstructures, followed by processing technologies available for production of useful components and products embodying these microstructures.

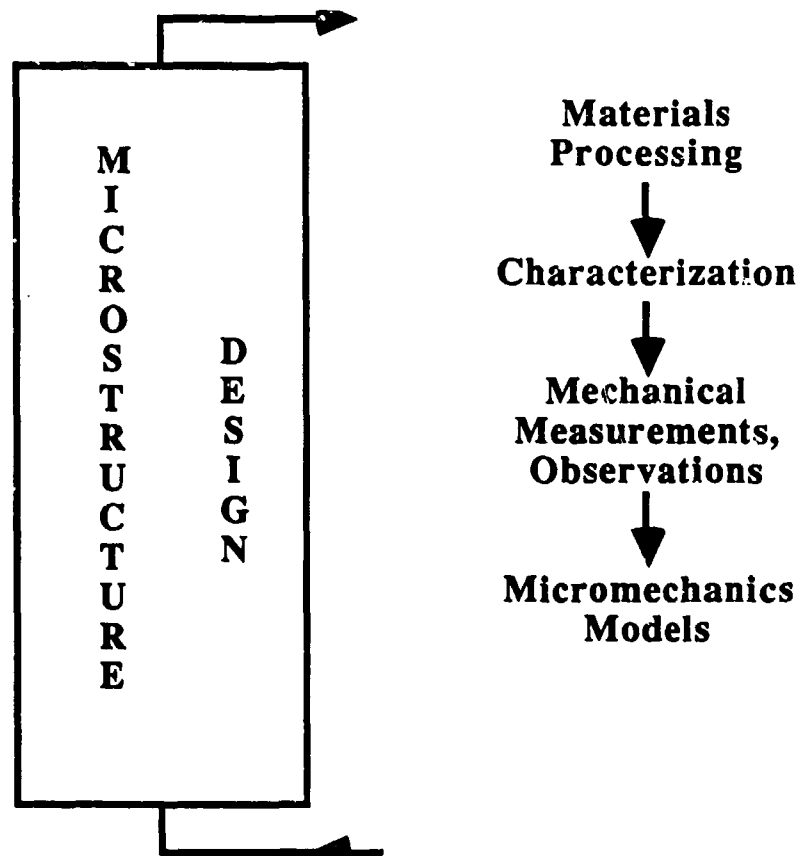


Figure 1. Approach for Development of Structural Composites

## STRUCTURAL PERFORMANCE

Brittle matrix composites require high structural integrity, in terms of fracture and creep resistance. Microstructural designs and models that indicate property optimizations are thus being investigated. For this purpose, studies of toughness, of creep resistance and of the role of matrix-reinforcement interfaces on properties are now in progress. The present state of each investigation and of the development of optimization concepts are summarized below.

### Toughening Concepts in Brittle Matrix Composites

Recent research concerning the toughening of brittle (intermetallic, ceramic) matrices by the incorporation of ductile dispersions and brittle fibers/whiskers has provided perspectives on property optimization (Budiansky, Evans). In particular, the development of small scale bridging models has progressed to the extent that certain trends in fracture resistance caused by bridging can now be rigorously assessed. For ductile particle toughening, the bridging contribution from the intact particles (Fig. 2) has been determined to scale directly with the product of the particle flow stress and the failure displacement. Ductile phases with maximum area under the uniaxial stress/strain curve (i.e., large work of fracture) would thus appear to contribute most effectively to toughening by bridging toughness. Comparison between theory and experiment on two ceramic/metal systems for which adequate experimental results exist ( $\text{Al}_2\text{O}_3/\text{Al}$ ,  $\text{WC}/\text{Co}$ ) has revealed however, that on the basis of bulk flow properties for the ductile phase (at the corresponding chemical composition), the measured toughening can only be rationalized by selecting a flow stress over 20 times larger than the uniaxial yield strength,  $\sigma_0$ . Finite element analysis (Mataga) has indicated that, while plastic constraint certainly elevates the stress appreciably above  $\sigma_0$  ( $\approx 6 \sigma_0$ ), stresses as high as  $20 \sigma_0$  over the full displacement range to failure are regarded as implausible. Complete understanding of ductile phase toughening thus remains to be established.

- Ductile Particles

$\text{Al}_2\text{O}_3/\text{Al}$

$\text{B}_4\text{C}/\text{Al}$

$\text{Al}_2\text{O}_3/\text{Ni}$



Toughness Increased From  
3 to 13  $\text{MPa}\sqrt{\text{m}}$

- Fibers/Whiskers

$\text{Al}_2\text{O}_3/\text{SiC}(\text{BN})$



Toughness Increased From  
3 to 10  $\text{MPa}\sqrt{\text{m}}$

Figure 2. Toughening

Several possibilities exist and are being studied; a) small particle effects on flow, b) residual stress effects, and c) crack-front trapping. The former is unlikely to fully account for the discrepancy, because large flow stress elevations have neither been observed nor predicted at the relevant micron-sized microstructural scale. Large residual stresses frequently exist, but their effect on ductile particle bridging has yet to be rigorously analyzed. Similarly, while trapping must occur, its magnitude is presently unknown. A continuing experimental/modeling activity, using experiments to provide the requisite insights, is expected to provide the next level of understanding regarding this toughening phenomenon. Some recent results on  $B_4C/Al$  systems (Aksay) processed by fluid metal phase penetration into the ceramic preform have begun to systematically investigate trends in toughness with the flow properties of the ductile phase. The preliminary observations indicate that 7075 alloy systems have the highest toughness and that such alloys, in the composite, are precipitation hardened (albeit that Zn is removed by evaporation during processing).

Toughening by brittle fibers/whiskers (Evans, Budiansky) is now known to be dominated by the relative local fracture resistances of the interface and matrix, by the fiber fracture properties and by the residual stresses. Furthermore, it is apparent from observations that several mechanism regimes of toughening exist (albeit that adequate mechanism maps have yet to be developed). Based on observations, the present hypothesis regarding toughening is that debonding first occurs along the fiber/matrix interface at the crack front, governed by the debond resistance of the interface (compared with the fiber). Such debonding, if sufficiently extensive, allows the fiber to remain intact in the immediate crack wake, and sets up the toughening. The extent of debonding also influences the dominant mode of toughening.

Three regimes have, thus far, been observed. Amorphous interphases provide limited debonding, leading to fiber failure in the wake at the end of the debond zone.

Toughening should then be explicable in terms of an elastic bridging model (Budiansky, Sanders ), with the fiber toughness being an important material parameter, as well as the debond length and the residual stress. At another extreme, materials with a graphite interphase have demonstrated extensive debonding and exhibit steady-state cracking. In this case, comparison between theory and experiment (Budiansky, Hutchinson, and Evans), based on frictional sliding along the debonded interface provides a self-consistent description of the mechanical behavior. Further, analysis of global fracture toughness (involving fiber as well as matrix fracture) reveals intrinsic correlations between steady-state matrix cracking behavior and toughening (Budiansky, Amazigo). Rigorous comparison between theory and experiment has yet to be conducted, largely because the appropriate set of measurements on uniaxially reinforced materials has not been performed. However, most of the recently processed, successful, fiber toughened brittle matrix composites exhibit intermediate behavior, characterized by classical pull-out on the fracture surface (Fig. 3). Such materials are typically processed by coating the fiber with a 'weakly' bonded thin layer (such as BN), followed by application of a reaction/diffusion barrier before incorporating the matrix. Fiber failure occurs in the crack wake, off the crack plane, at appreciable multiples of the fiber diameter. Frictional sliding during pull-out then contributes importantly to the toughness, leading to characteristics wherein the crack growth resistance increases continuously with crack extension. The slope of the resistance curve is influenced by the statistics of fiber failure, by the interface sliding resistance and the residual stress. Analysis has indicated that fibers with tensile strengths having large standard deviation (and high mean) enhance the toughening, by causing the fiber to fail at relatively large distances from the crack surface. Additionally, observations reveal that the mean pull-out length decreases as the interface 'strength' increases. However, comparisons between theory and experiment are too limited to provide definitive predictions of trends in fracture resistance

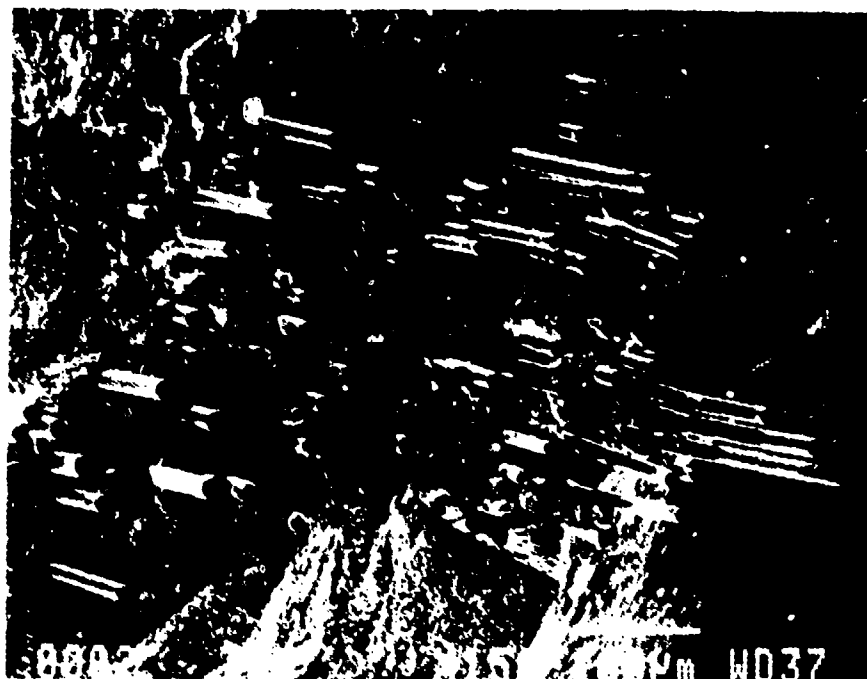


Figure 3. Fiber pull-out in a SiC reinforced  $\text{Al}_2\text{O}_3$  (Lanxide<sup>TM</sup>) material having a toughness of  $\sim 18 \text{ MPa}\sqrt{\text{m}}$ .

with the properties of the the interface and fiber. Nevertheless, experimental measurements have established that toughnesses of order 20 MPa√m are consistently attainable within this toughening regime. Further studies of fiber toughening should emphasize a superior understanding of relationships between interphase properties, debond extent, location of fiber failure and pull-out resistance for composites of this type. Studies on heat treated Lithium-Alumino-Silicate/SiC from UTRC and on Al<sub>2</sub>O<sub>3</sub>/SiC from Lanxide should provide insight in this regard.

#### Creep Resistance of Composites

The creep behavior of composites has been explored for continuous and discontinuous microstructural extremes (McMeeking). Composites that contain continuous elastic reinforcements (weaves, laminates, preforms) exhibit creep strains limited by the elastic strain of the reinforcing network. The matrix creep resistance simply governs the rate at which the saturation strain is approached. The saturation strain for such composites can be less than the allowable strain for the component, whereupon the creep resistance of the matrix is of minor importance. The only issue of concern is then the material toughness (Toughening Concepts). Consequently, where possible by virtue of processing capabilities, continuous network composites are preferred.

Composites containing discontinuous reinforcements have a creep resistance governed by the size, shape and contiguity of the reinforcing phase, and the slip resistance of the interface. At one scale, small stable dispersoids induce a creep threshold stress equal to a fraction,  $\lambda$ , of the Orowan stress, with  $\lambda$  governed by relaxation effects at the dislocation core in the interface. Small dispersoids that resist coarsening and have high interface diffusivities are thus preferred. At the other extreme, large isolated (dilute) reinforcements directly modify (reduce) the matrix creep rate, by a ratio that depends on volume fraction, shape and interface slip resistance. Trends are known for bonded spheres and aligned rods (but the effects of random rods and discs

and of interface sliding are unsolved, except for linear matrices). However, experimental results for aligned rod reinforced composites deviate from predicted trends and, in fact, exhibit appreciably greater creep resistance than dilute models would predict (Fig. 4). The deviations suggest either large transient strain effects or interlocking networks. Further study of these latter issues is clearly important if the observed creep resistant characteristics are to be understood and optimized.

#### Interfaces and Interface Failure

Brittle matrix composites having high toughness require either strongly bonded interfaces for ductile reinforcements, or weakly bonded interfaces for brittle (fiber) reinforcements. A fundamental understanding of interface debonding is needed to design composites with the appropriate interface characteristics. The debonding of interfaces between metal and ceramics has begun to be investigated at various levels including: crack growth measurements, calculations of bond energies and experimental studies of atomistic structures and chemical gradients. Present understanding is limited, although methods exist that allow systematic investigation.

Studies of fracture resistance (Rice) have recently established a complex stress intensity factor,  $K$ , formulation for determining the locus of fracture resistance in small scale yielding (Fig. 5), based on critical values of the modulus  $|K_c|$  and the phase angle,  $\psi$ . Calculation of plastic zones in small scale yielding (Shih) have also begun to establish non-dimensional parameters that govern crack tip fields. Furthermore, some test specimens that allow measurement of  $|K|$  vs.  $\psi$  have been designed and calibrated (Evans). Systematic progress in measuring the fracture resistance is thus expected. The results of these studies should yield a measure of the basic debond energy of the interface as a function of phase angle, once faceting effects, etc., have been decoupled. It would then be informative to compare the measurements with calculations of bond energies.

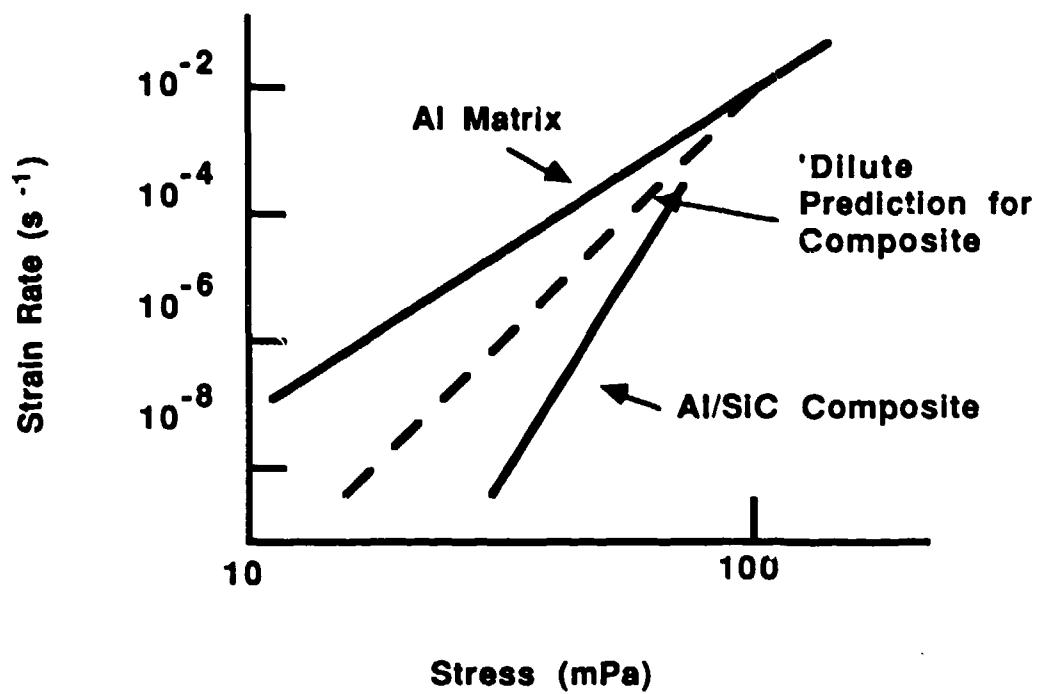


Figure 4. Creep results for Al/SiC Composites

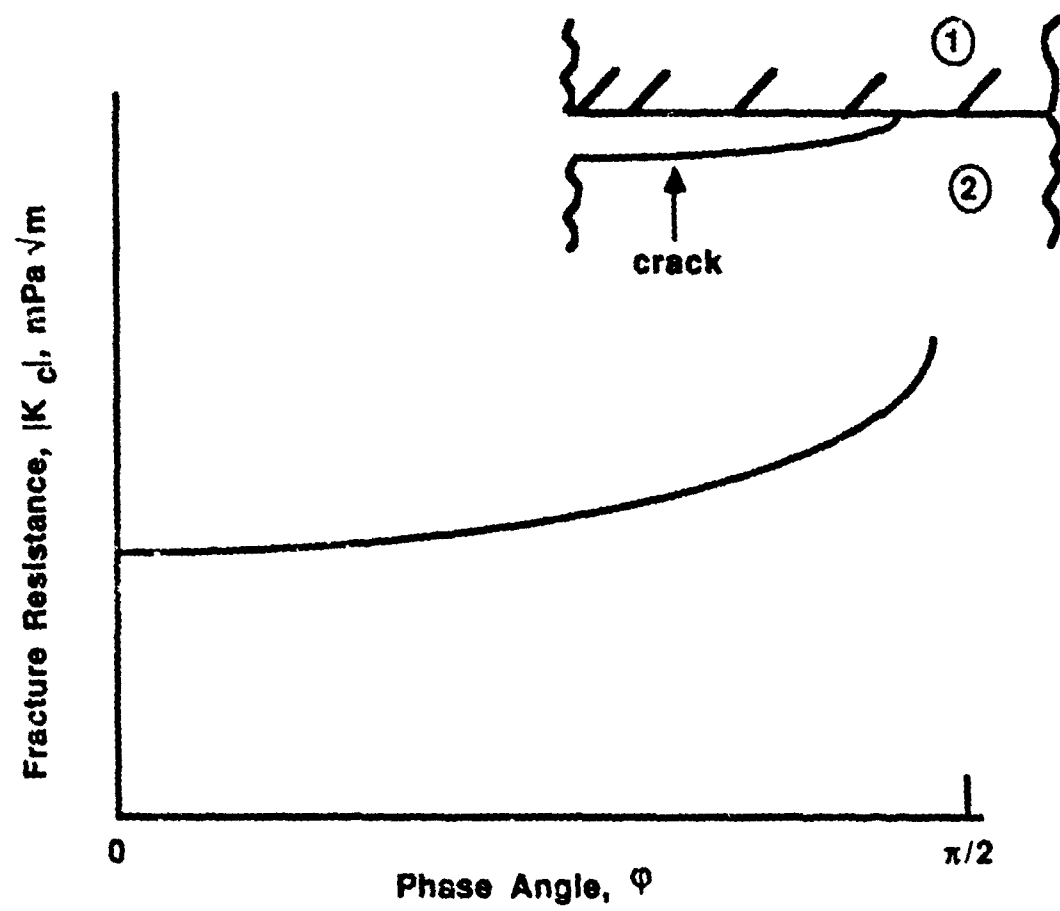


Figure 5. Fracture Resistance Locus For Interface Cracks.

For bond energy analysis, it is recalled that the energy required for separating interfaces is the difference between the surface energy of the debonded unrelaxed surfaces and the energy of the bonded system (which includes the interfacial energy). Furthermore, since segregation typically occurs at the interface, the debond energy must be the difference between the energy of the segregated interface and the energy of the surfaces covered with the segregants (Rice). The most rigorous calculations of bond energies involve a quantum-mechanical ab initio approach. Such calculations are normally computer intensive. However, newer, more efficient, schemes (Car and Parrinello) that combine molecular dynamics with density functional theory should allow calculation of the energetically most favorable structures, and the bond energy. Such calculations are in progress. 'Chemical' approaches also describe the bonding and the modifications of bonding at interfaces. In the course of these calculations the electron density distribution is calculated and the overlap of different orbitals directly correlated to the bonding between atoms. This approach is seemingly able to predict certain properties of interfaces, e.g., the cohesion at grain boundaries in intermetallics (Eberhart). The approach is often insightful. However, the numerical quality of the calculations is debatable, because the atomistic structure is neglected.

Experimental studies on "model" interfaces (Nb/Al<sub>2</sub>O<sub>3</sub>, Ti/Al<sub>2</sub>O<sub>3</sub>, Ni/Al<sub>2</sub>C<sub>3</sub>, Ag/CdO) have revealed (Ruhle) that chemical reactions may occur at interfaces and that the formation of reaction products, as well as the morphological stability, depends strongly on the reaction path. Structural studies by TEM and HREM have indicated that interfaces between oxides and metals seem to be energetically more stable when the interface plane is parallel to a plane of the oxide having the highest area density of oxygen. [(0001) in sapphire and (111) for fcc binary oxides]. HREM studies at the interface of internally oxidized (Nb, Al) and (As, Cd) alloys have also demonstrated that an oxygen plane of the oxide abuts the interface. These studies provide a basis for bond

energy calculations and, eventually, an understanding of the interface fracture resistance.

## PROCESSING

The processing of structural metal (e.g., intermetallic) and ceramic matrix composites is based on microstructural design guidance received from the micromechanics efforts described in the previous sections. Some of the available process "pathways" are listed in Tables 1 and 2. These lists are not exhaustive but emphasize these processes which were reviewed in this workshop.

**TABLE 1**

### **PROCESSING OF METAL MATRIX COMPOSITES**

**Atomization (rapid solidification) of metals (e.g., intermetallics) and metal matrix composites followed by consolidation (HIP/extrusion) or plasma deposition techniques.**

**Preparation of liquid matrix composites followed by shape forming (e.g., squeeze casting).**

**Liquid infiltration of, presintered ceramic fiber preforms and/or particulates.**

**TABLE 2**

**PROCESSING OF CERAMIC MATRIX COMPOSITES**

- **Chemical vapor infiltration (CVI)**
- **Metal Infiltration coupled to metal/gas (e.g. oxidation) reaction process-Lanxide™**
- **Metal Infiltration into dense 3-D preforms**
- **Colloidal techniques coupled to filtration.**

**Metal Matrix Composites**

**i) Atomization - Rapid Solidification Processing**

Emphasis was placed on rapid solidification of a new family of intermetallics based on the TiAl system. Rapid solidification processing is used to generate new "pathways" to microstructures not available in conventional ingot metallurgy. The binary Ti-Al system can be used as an illustrative example of the range of microstructures that are possible when nucleation and growth kinetics of different phases compete in the formation of rapidly solidified structures. It should be noted that these structures form the matrices of the composites formed by consolidation through hot isostatic pressing (HIP) and extrusion.

The fundamental issues of thermodynamics and kinetics were addressed (Mehrabian, Levi, Perepezko, Chang, and Boettinger). Two slightly different versions of the Ti-Al phase diagram are shown in Figures 6 and 7. In Figure 6 the conventional (slow solidification of an Al-50 at% Ti alloy would follow a "pathway" which would result

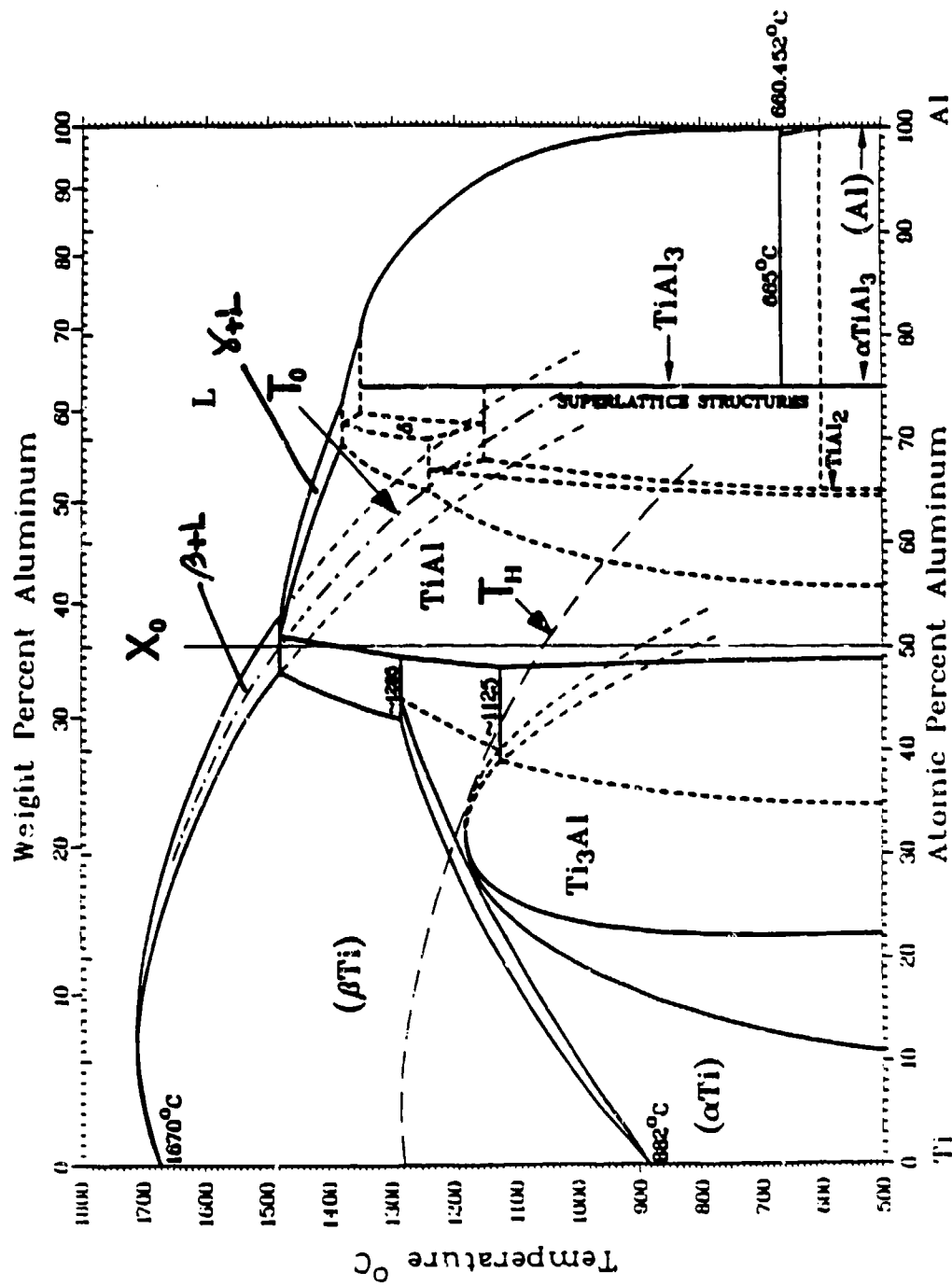


Figure 6. The System Titanium - Aluminum.

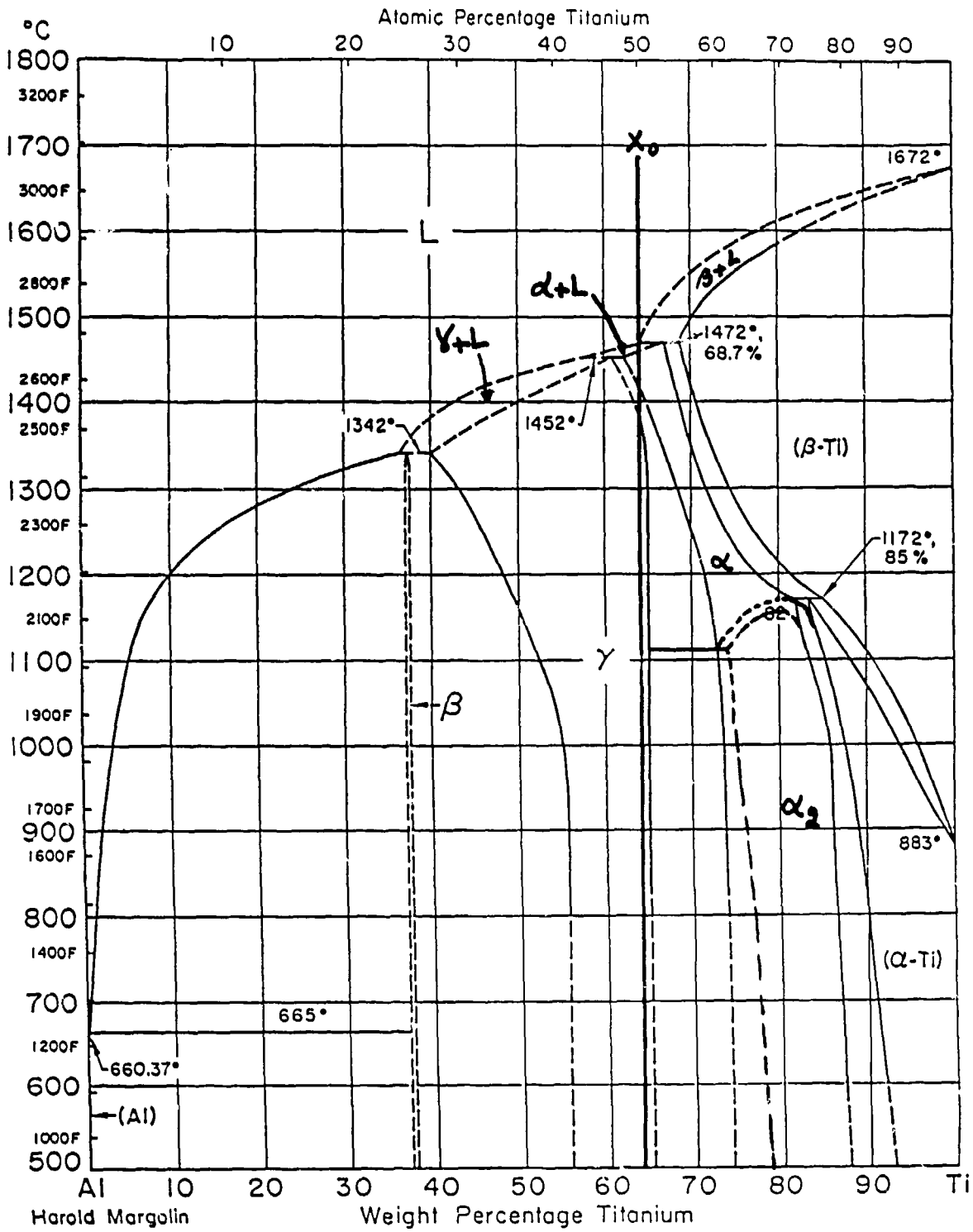
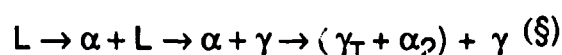


Figure 7. Al-Ti Aluminum - Titanium

in the formation of  $\beta$ (BCC) dendrites followed by solidification of  $\gamma$ (FCT) in the interdendritic regions below the peritectic temperature. On the other hand, the phase diagram in Figure 7 shows that  $\alpha$ -dendrites should form first followed by solidification of  $\gamma$  in the interdendritic regions. Examples of observed microstructures in arc-button melted ingots are shown in Figure 8 where hexagonal  $\alpha$ (HCP)-dendrites protrude in the porous region in the center of the ingot. The remaining liquid in this region was depleted to feed interdendritic shrinkage in the adjacent areas of the ingot. Figure 8b shows a higher magnification micrograph of dendrite arms which were subsequently transformed to ordered  $\alpha_2$  and  $\gamma$  lath structure. TEM analysis of the lath regions, Figure 9, revealed that the structure exhibits two  $[110]$  variants of the  $\gamma$ -phase that are related by a twin relation (twinning of a  $\{111\}$  type plane) as well as  $[1210]$  variant of  $\alpha_2$ . A similar study of the interdendritic regions revealed that they consisted only of the  $\gamma$ (FCT)-phase with no twinning, although such regions often contained many low angle boundaries, Figure 10. Composition profiles showed the twinned  $\gamma$  and  $\alpha_2$  regions had an average composition of 47 at% Al whereas the interdendritic  $\gamma$  had an average composition of 55 at% Al. This is in agreement with the expected solute redistribution of the peritectic reaction:



Rapidly solidified powders of Ti-50 at% Al alloy show a range of microstructures as shown in Figure 11 and 12. Some coarse powders show similar microstructures to that of the input, but with a reduction of the amount of  $\gamma$  formed directly from the liquid, Figures 11(c) and 11(d). The secondary dendrite arm spacings (7 to 10  $\mu\text{m}$ ) are much smaller than those found in the ingot (20-25  $\mu\text{m}$ ) Figure 11(a) and 11(b). Average composition of the phases are 49 at% and 53 at% Al for the transformed primary and  $\gamma$  - where  $\gamma_T$  denotes  $\gamma$ -phase formed by a solid-state transformation

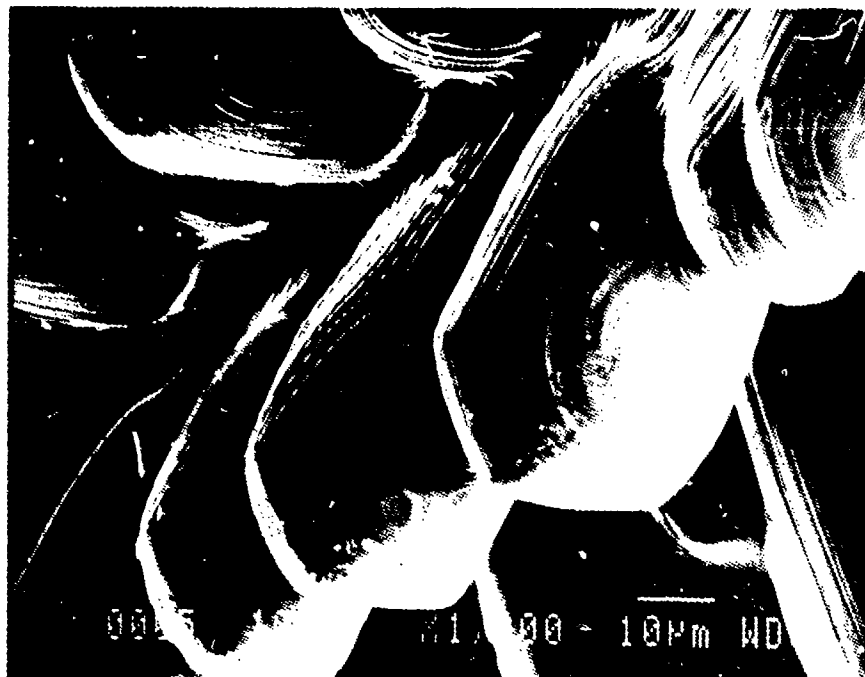
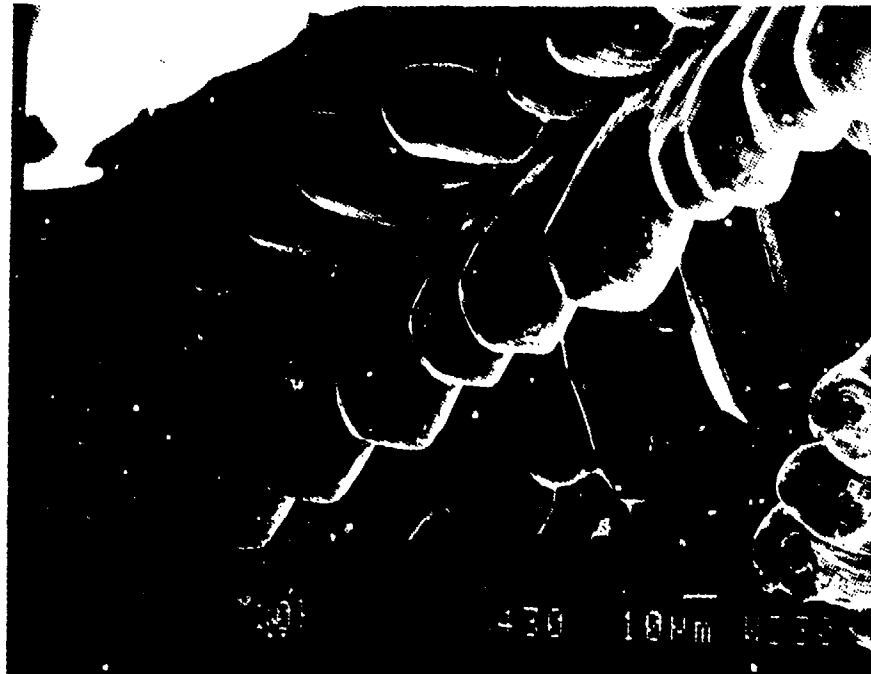


Figure 8. SEM views of primary  $\alpha$ (HCP) dendrites formed in Ti-50 at % Al arc-button method ingots (from UCSB/URI, Mehrabian and Levi).

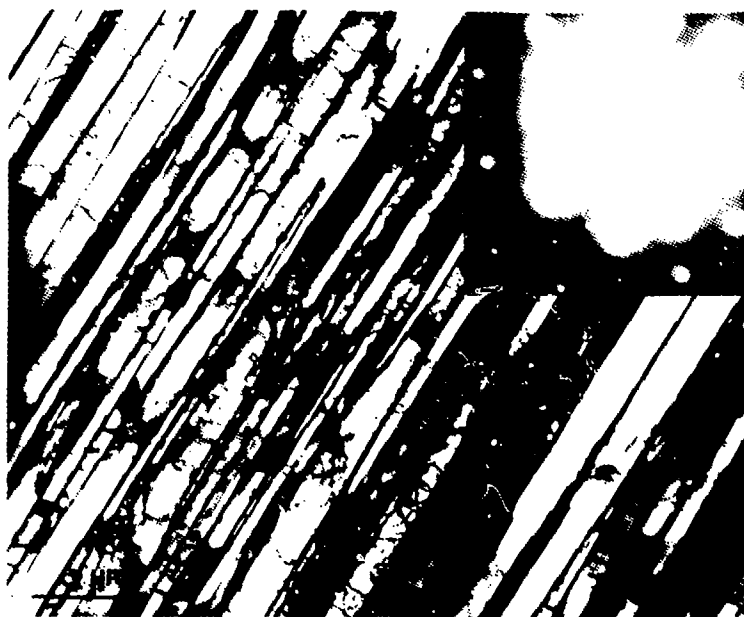


Figure 9. Lath structure inside a primary  $\beta$  dendrite containing twinned  $\gamma$  and  $\alpha_2$ . Zone axes are  $[110]_\gamma$ ,  $[110]_\gamma$ ,  $[1210]_{\alpha_2}$  (from UCSB/URI, Mehrabian & Levi).



Figure 10. Interdendritic  $\gamma$  phase showing the presence of many low angle boundaries and  $[112]_\gamma$  convergent beam diffraction pattern. All the subgrains are within  $1^\circ$  of this axis (from UCSB/URI, Mehrabian & Levi).

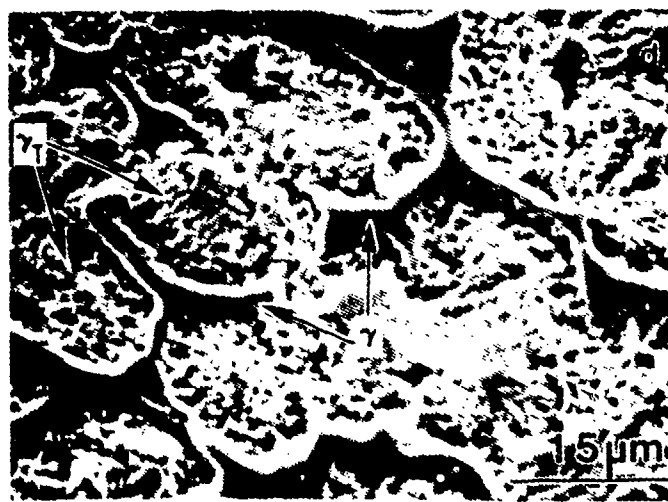


Figure 11. Microstructures resulting from the peritectic solidification of Ti-50 at% Al showing transformed  $\alpha$  dendrites surrounded by  $\gamma$ . (a) and (b) are from the arc-melted buttons while (c) and (d) are from coarse powders (from UCSB/URI, Mehrabian & Levi).

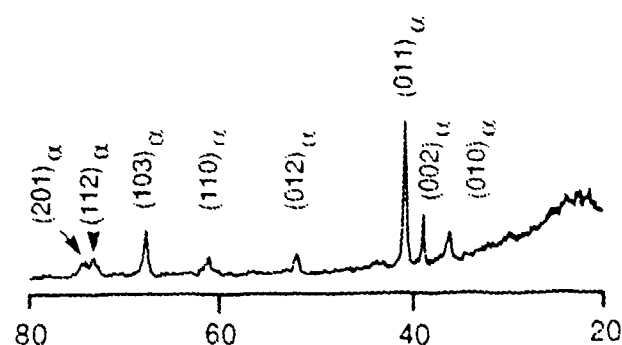
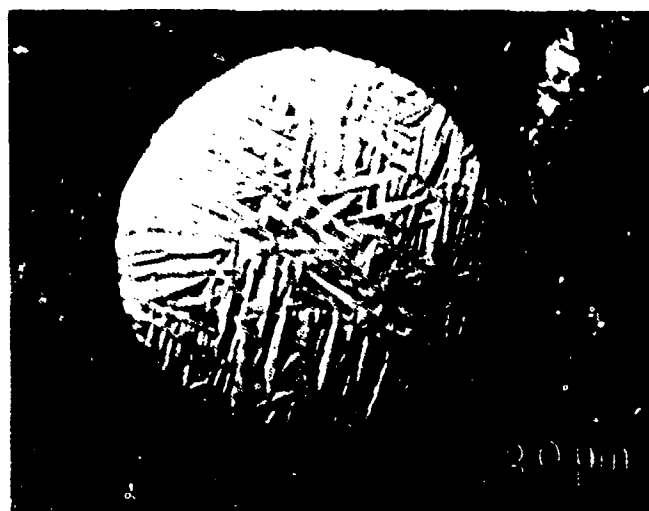
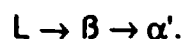


Figure 12. EHD powder microstructures suggesting solidification to a single phase  $\beta$  which transforms martensitically to  $\alpha'$  upon cooling. X-ray diffraction of 53-75  $\mu\text{m}$  powders shows reflections corresponding to hexagonal  $\alpha$ -Ti but no superlattice peaks from  $\alpha_2$  or  $\gamma$  (from UCSB/URI, Mehrabian and Levi).

interdendritic constituents, respectively. This is consistent with a solidification "path" in which the thermally activated nucleation of  $\gamma$  from the liquid is suppressed to lower temperatures by the faster cooling rates achieved in the droplets. Since this interdendritic  $\gamma$ -phase does not nucleate easily at the peritectic temperature, a metastable extension of  $\alpha$ -phase field is produced.

In addition to the transformation "path" described above, a second microstructure is found in rapidly solidified powder particles. This involves solidification to single phase  $\beta$ , followed by a martensitic transformation of  $\beta$  to hexagonal  $\alpha'$ , producing the microstructure shown in Figure 12. X-ray diffraction confirms sole presence of the HCP phase for powders of the finer sizes, although it is unclear if this subsequently orders to  $\alpha_2$  upon cooling. The powders of this type appear to be homogeneous in composition. However, there is a tendency for these powders to have a lower overall aluminum content. The origin of this is still under investigation. The solidification may then be expressed as:



A technologically interesting outcome of this work is that by appropriate manipulation of composition and rapid solidification process variables one may produce different microstructures for subsequent consolidation into desired shapes (i.e., thin sheets). Of course, the processes involved can include production of particles containing stable rare-earth oxides precipitated from the melt (Anderson and Sastry) or starting with a liquid slurry that already has particulates which have previously formed through the XD™ process (Venables). Furthermore, the more brittle  $\gamma$ -phase intermetallic can be premixed with other ductile particles, prior to consolidation, to obtain the tougher microstructures described in the previous section of this report. Figure 13 shows an example of the role ductile niobium particles play in a brittle TiAl matrix (Mehrabian and Evans). Indentation cracks in the matrix are arrested by the ductile

Hipped & Forged

Ductile Phase: 20 v/o Nb

Matrix: TiAl



Top View



Side View



End View



Figure 13. Indentation Crack Arrest in Intermetallic - Metal Composites.

niobium particles. Fracture toughness measurements in a number of similar systems have shown significant improvements through the incorporation of these particles, Figure 14 (Sastry). A major impediment to this type of toughening is interface interaction between the matrices and the ductile phases during high temperature consolidation and subsequent heat treatment (see right hand side of Figure 14). Theoretical phase diagram calculations coupled with diffusion couple experiments are underway (Chang and Perepezko) to identify ductile phase compositions that would remain in equilibrium with the Ti-Al matrices at high temperatures. Finally, the beneficial effect of stable second phase dispersoid reinforcements and coarse grain structure on the creep properties of rapidly solidified and consolidated titanium aluminides is shown in Figure 15 (Sastry).

Rapid Solidification by plasma deposition (RSPD) using an RF plasma generator (A. Johnson) is an alternate technique for direct production of composite containing fibers. Figure 16 shows a schematic of the process. Powders of the desired composition are fed into an RF plasma gun and deposited into a rotating mandrel in vacuum. Filaments of the desired fiber are wound on the mandrel prior to deposition to produce monotapes. Figure 17 shows an example of plasma sprayed titanium alloy monotape reinforced with silicon carbide fibers which was subsequently cut, stacked, canned and hot isostatically pressed. Representative tensile properties of plasma sprayed titanium alloys with and without silicon carbide reinforcement are shown in Figure 18. The advantage of this process is that it combines rapid solidification of molten droplets (on the mandrel substrate) with the incorporation of continuous fibers. Further studies are underway to determine the integrity of the microstructures produced as well as the critical question of matrix/fiber interface interactions with or without coating.

#### ii) Bulk Liquid Processing

Metal matrix composite preparation techniques utilizing bulk liquid can be classified into two categories. In the first technique (Mehrabian) fibers and particulate

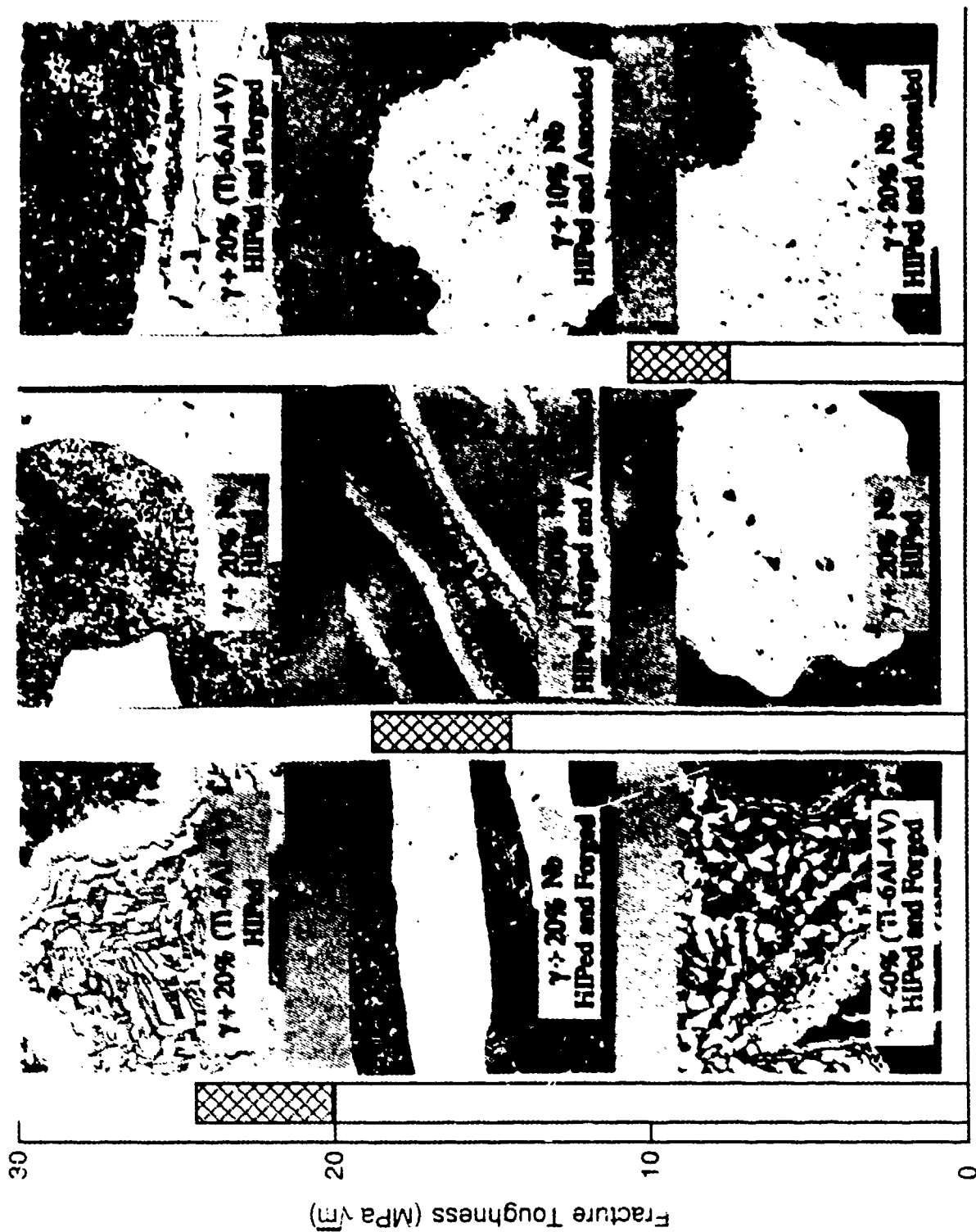


Figure 14. Effect of Composition and Processing on Fracture Toughness of Ductile Phase Reinforced Titanium Aluminides (from Sastry).

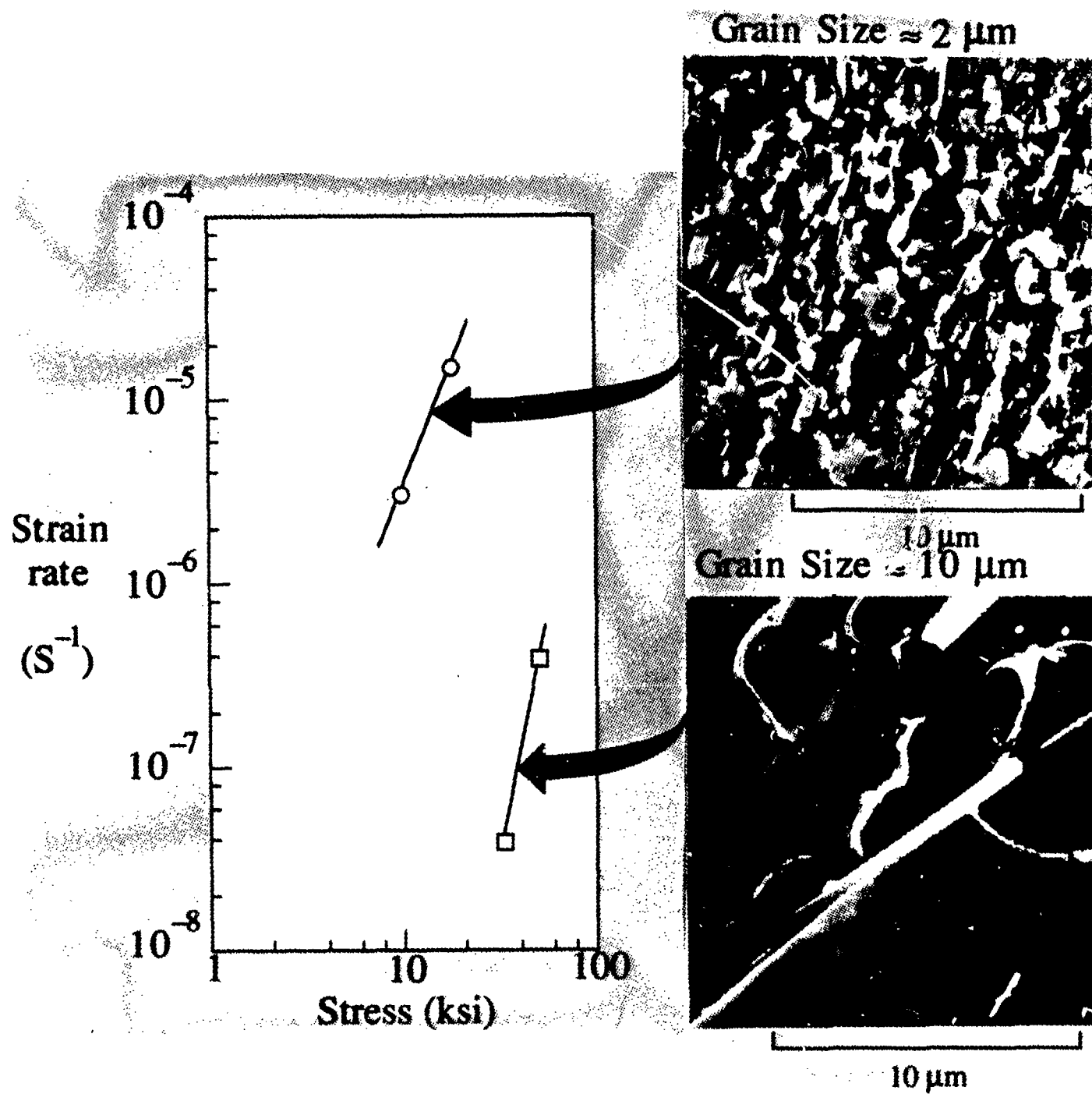


Figure 15. Effect of Grain Size and Reinforcement Size on Creep of Titanium In Situ Composites (from Sastry).

# MMC Fabrication

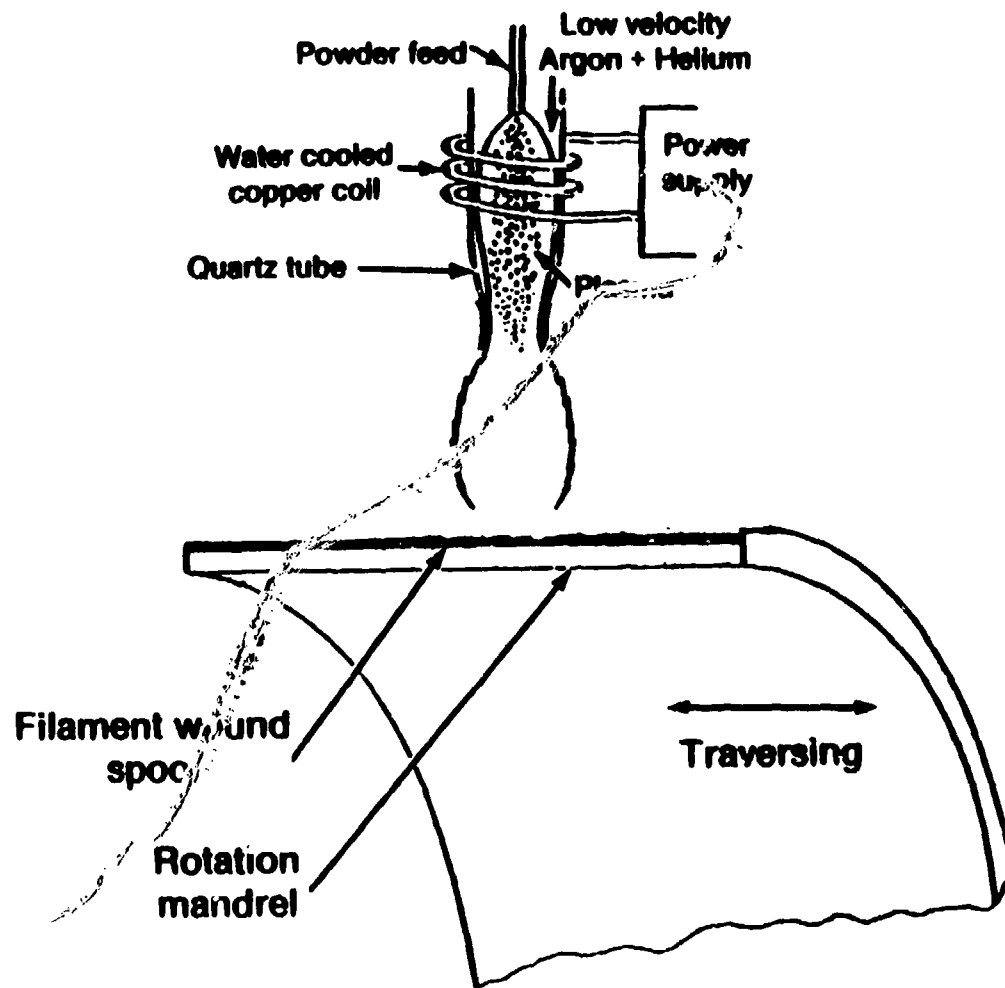


Figure 16. Schematic illustration of the RSPD process-or preparation of metal matrix composites (from A. Johnson).



Figure 17. Titanium Aluminide MMC Monotape (from A. Johnson).

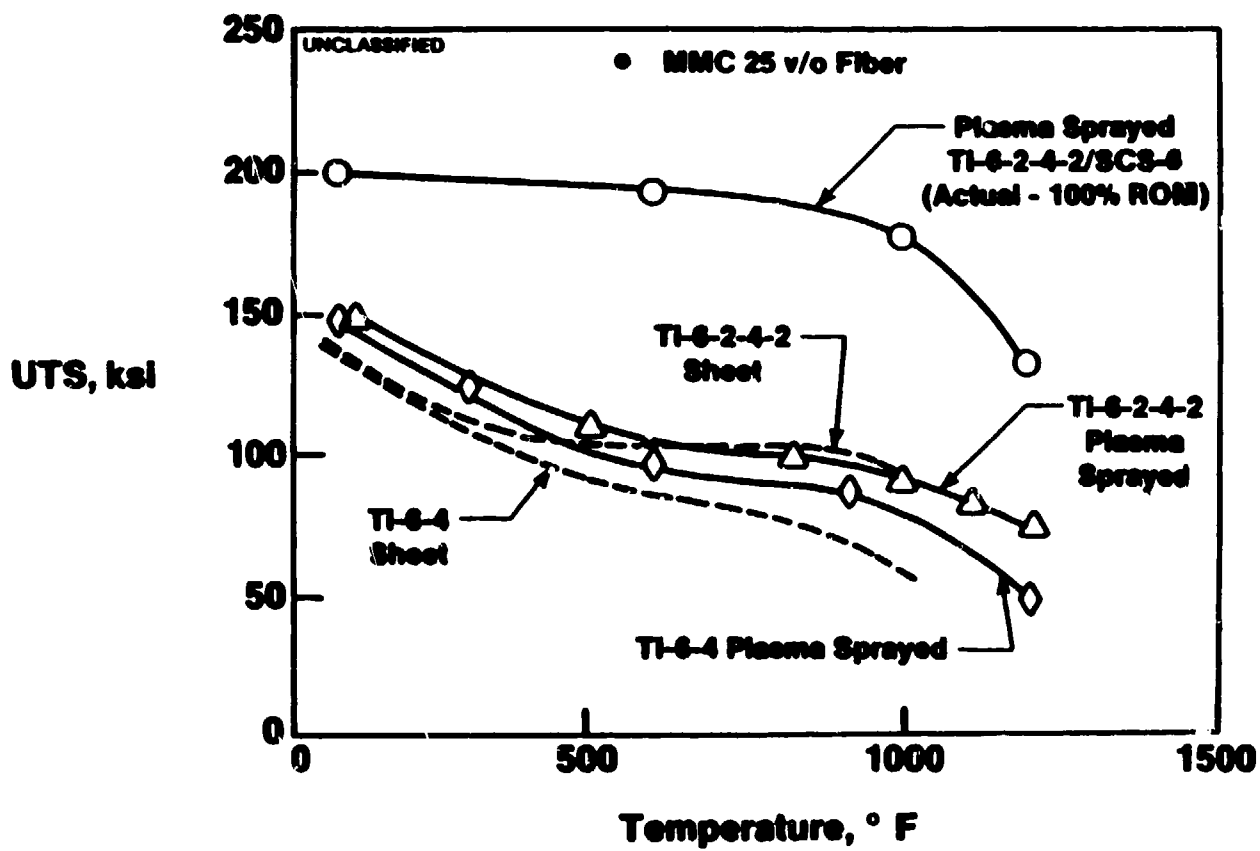


Figure 18. Plasma Sprayed "Neat" Foil and MMC Data (from A. Johnson).

are stirred into a liquid matrix and formed into shapes directly or cast into ingots for subsequent liquid or solid forming operations. Figure 19 shows a schematic of the compositing technique. Figure 20 depicts a method for increasing the volume fraction of particulate and fiber additions by pressurization of the composite above a ceramic filter. Liquid metal infiltrates the ceramic while the fibers are retained above the filter. Fiber content in the composite is thus increased while the forming operation produces a two dimensional planar - random fiber alignment. Figures 21 and 22 show SEM micrographs of aluminum alloy/FP  $\text{Al}_2\text{O}_3$  fiber composites. In Figure 23 the matrix has been etched away to show fiber integrity, alignment and concentration in the composite. The critical issue in this method of composite processing is to obtain a strong matrix/fiber bond without excessive interface interaction. Initial wetting (assisted by stirring) is essential for fiber incorporation, however, time and temperature of fabrication should be kept to a minimum to inhibit formation of interface phases. Figure 23 shows formation of  $\text{MgAl}_2\text{O}_4$  spinel when FP  $\text{Al}_2\text{O}_3$  fibers were incorporated in an Al-4 wt% Mg alloy liquid matrix.

The second technique for preparation of composites in a bulk liquid is the XD<sup>TM</sup>® technique developed at Martin Marietta (Venables), Figure 24. In this case small particles ( $<1\mu\text{m}$ ) of hard phases such as  $\text{TiB}_2$ , TiN etc. are formed in-situ in such a manner that the surface of the particles is never exposed to air. The matrix containing a high concentration of particles can then be incorporated into a second matrix (e.g., TiAl) without contamination. Improved high temperature properties for TiAl have now been demonstrated in a classified program. As previously noted, one method of improving room temperature ductility of brittle intermetallic composites is to incorporate ductile particles. Another method is to incorporate whisker-like reinforcements that exhibit a relatively weak bond to the matrix with the expectation that the fiber pull-out mechanism, successfully employed in toughening ceramic composites would, likewise serve to

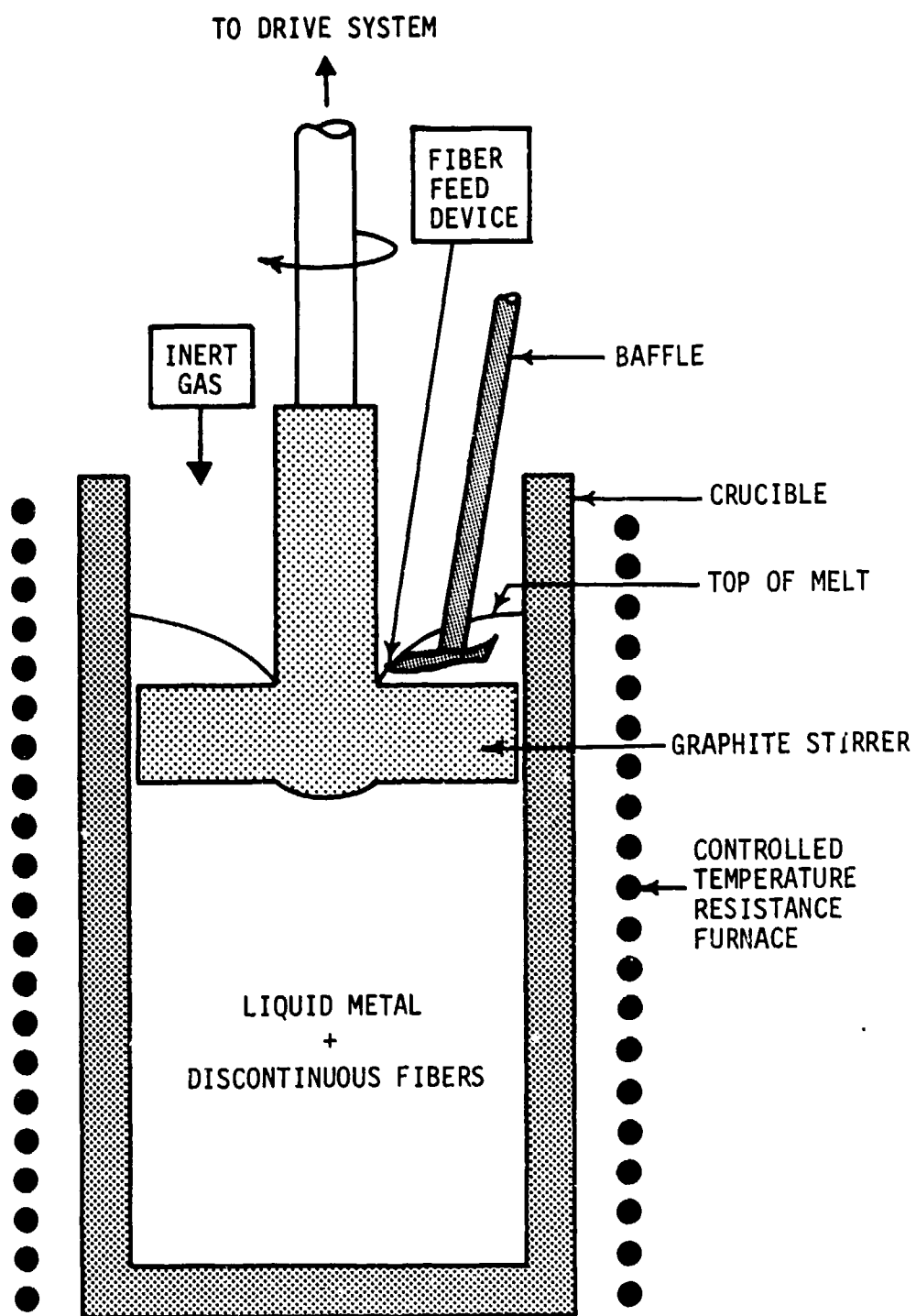


Figure 19. Schematic illustration of metal matrix compositing technique in which fiber and/or particulates are stirred into a bulk liquid (from Mehrabian).

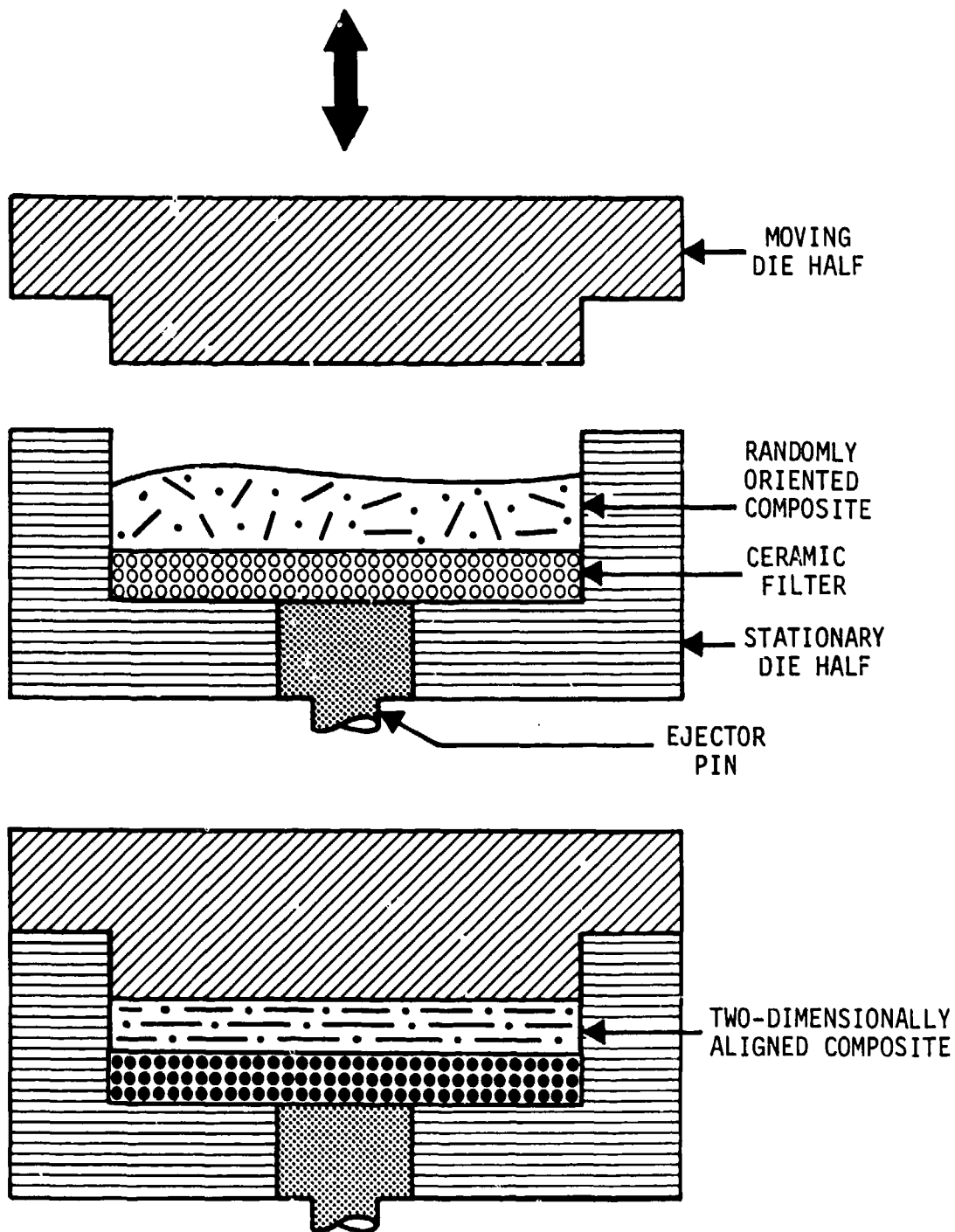
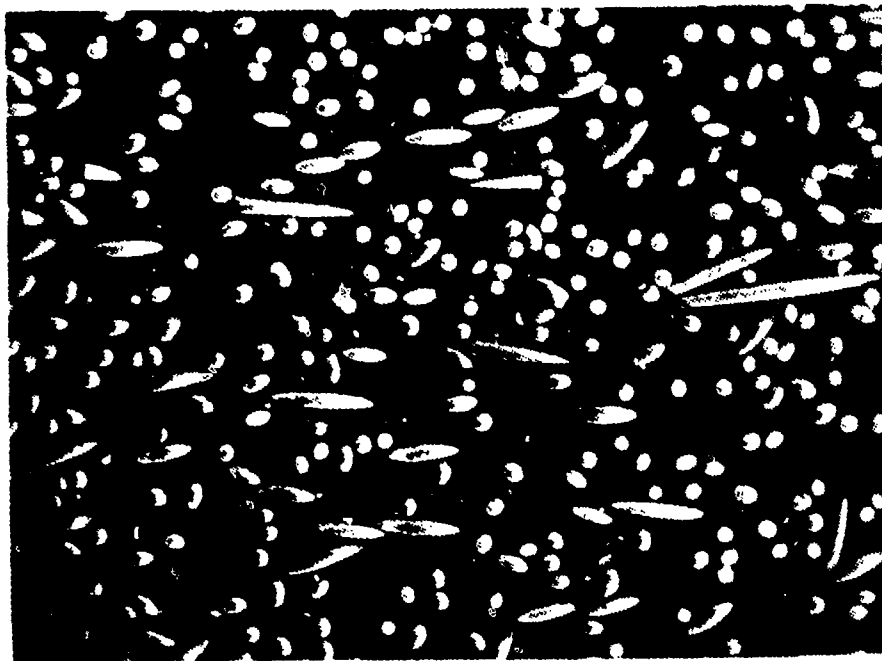
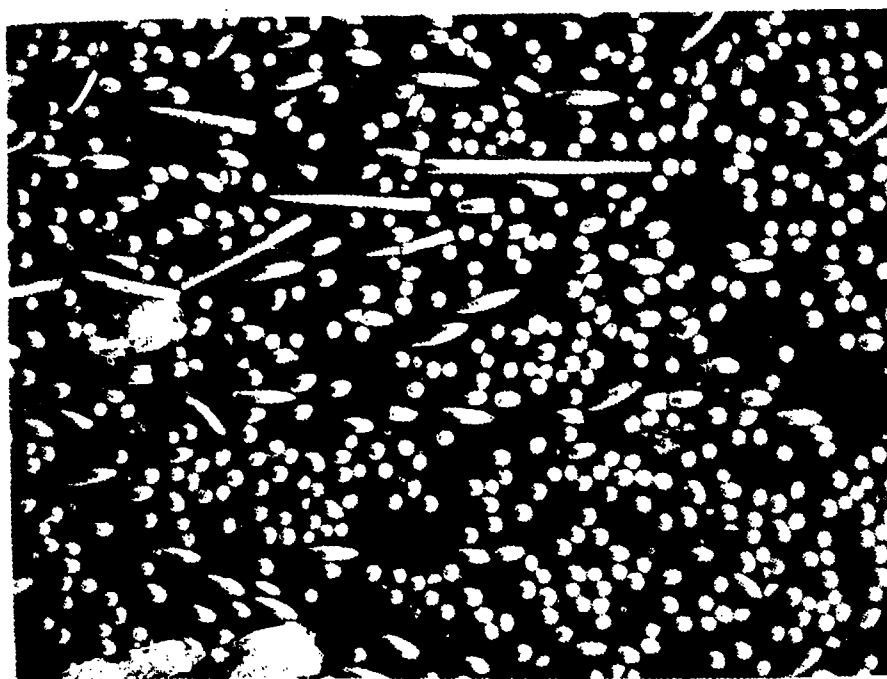


Figure 20. Schematic of the forging dies and ceramic filter used to two-dimensionally (planar-random) align the fibers in the composite (from Mehrabian).



(a)

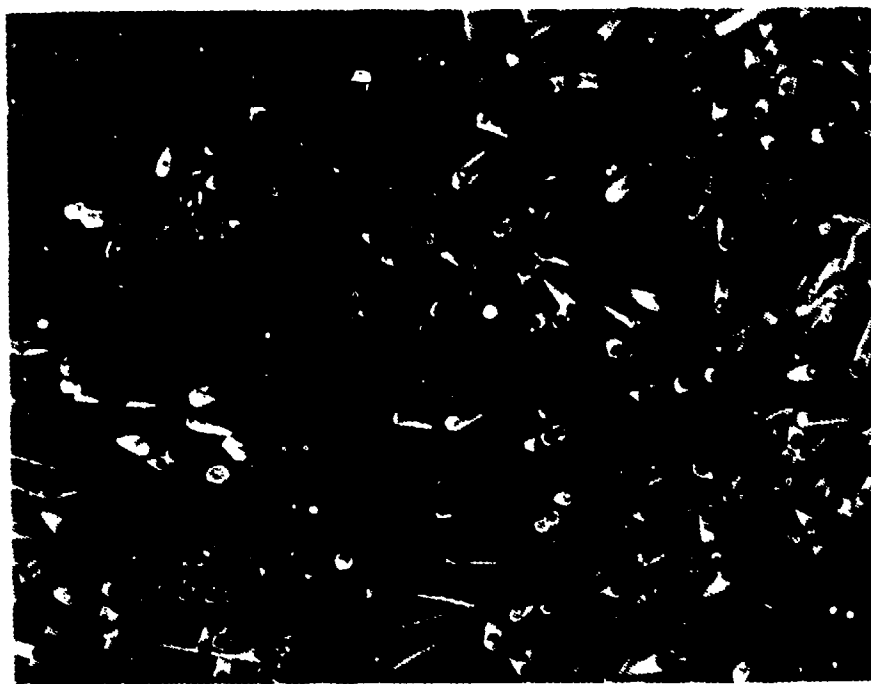


(b)

Figure 21. Typical microstructures of the side view (vertical cross-section) of a planar-random fiber composite part. (a) shows a 14 v/o  $\text{Al}_2\text{O}_3$  fiber composite at 100x and (b) shows a 23 v/o  $\text{Al}_2\text{O}_3$  fiber composite at 100x (from Mehrabian).



(a)



(b)

Figure 22. Electroetched vertical sections of a 23 v/o  $\text{Al}_2\text{O}_3$  fiber planar-random composite part. In (1) and in (b)  $\sim 50\mu\text{m}$  and  $\sim 1000\mu\text{m}$  of the matrix has been dissolved away, respectively. (a) and (b) are at 100X (from Mehrabian).

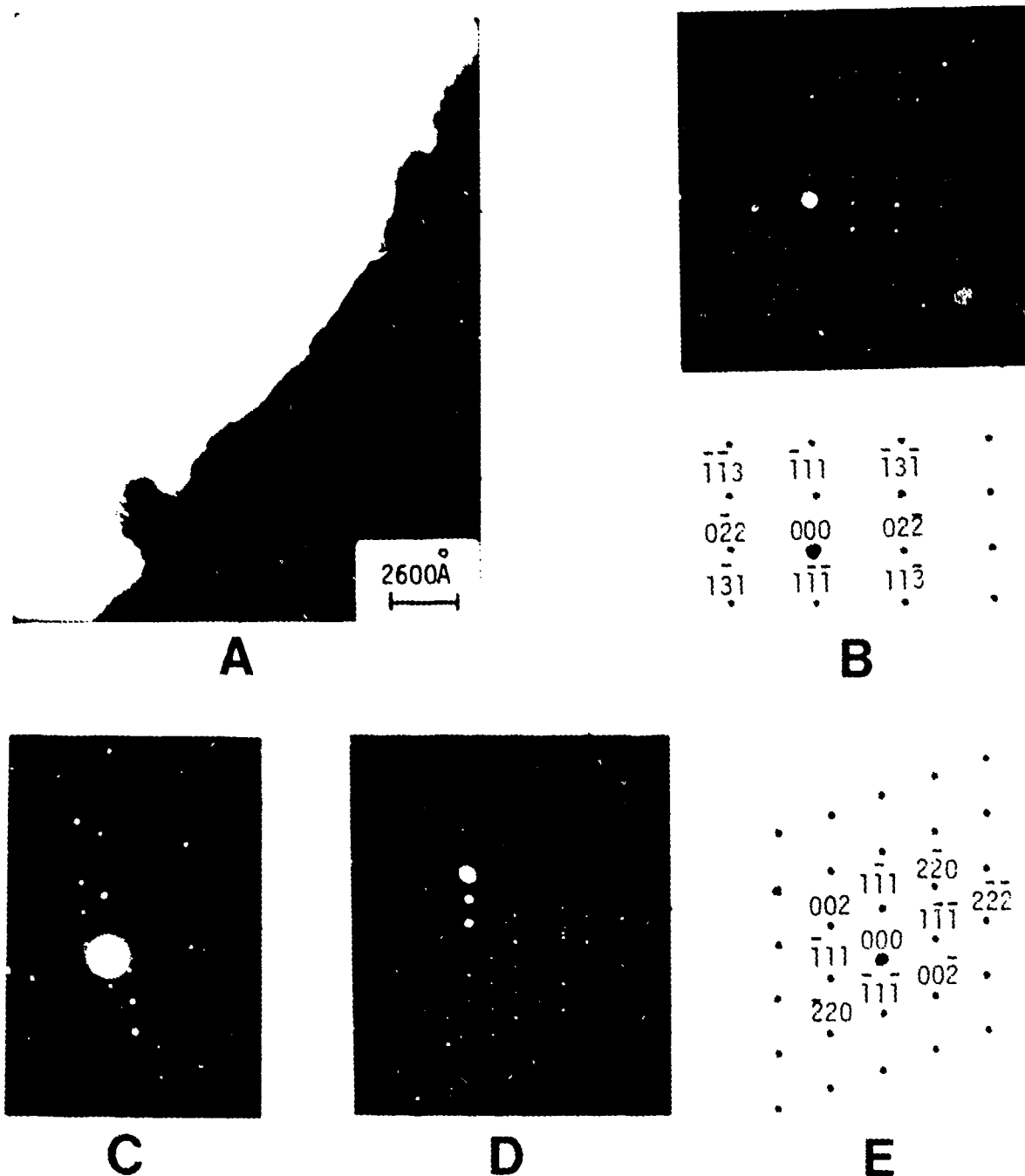


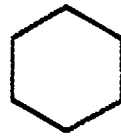
Figure 23. Observations relating to spinel diffraction patterns (from Mehrabian).

- Profile of fiber isolated from bulk liquid processed composite.
- Diffraction pattern from one point on fiber edge with indexing as spinel, Z.A.  $[211]$ .
- Diffraction pattern from another point on fiber edge.
- Diffraction pattern from  $MgAl_2O_4$  powder.
- Indexing of D and C as spinel, Z.A.  $[110]$ .

## UNIQUE FEATURES OF XD™ PROCESS

### CONVENTIONAL COMPOSITES

LARGE CERAMIC PARTICLES WITH  
POOR METAL/PARTICLE BONDING



→ Oxidized/contaminated  
surface layer



→ Clean interface

### XD™ ALLOYS

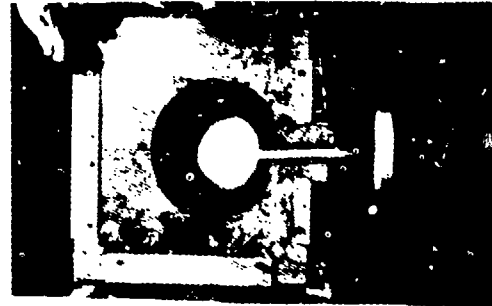
PROCESS YIELDS FINE DISPERSOIDS WITH  
DIRECT DISPERSOID/METAL CONTACT

Coarse particles  
and weak interface

→ Low ductility/low fracture  
toughness

Fine particles and  
strong interface → High ductility/fracture  
toughness

### CASTING PROCESS



### PARTICLE SIZE AND SHAPE CONTROL



Submicron



Micron



Whiskers

### CHARACTERISTICS

- Applicable to many metal matrices
- Ti, Al, Ni, Mg, Cu, Fe, Nb
- Variety of dispersoids
- Significant modulus increases
- High ductility/fracture toughness
- Improved fatigue resistance
- High-temperature stability
- Increased wear resistance
- Weldable
- Opportunity for hybrid systems,  
i.e., long-fiber-reinforced XD™ Alloys

Figure 24. Ti-Based XD® Composites (from Venables).

improve room-temperature toughness of titanium aluminides. The XD™ process has recently been employed to produce whisker materials that might exhibit an inherent weak interfacial bond to the matrix. Figure 25 shows fracture surface of a cast TiAl composite in which whiskers protrude from the matrix, suggesting, a weak bond to the matrix.

### iii) Liquid Infiltration

The final method discussed is preparation of metal matrix composites by infiltration of sintered ceramic fiber and/or particulate preforms with liquid metals alloys. In this process (Mehrabian) an apparatus similar to that shown in Figure 20 is used except the ceramic filter is now the preform into which a liquid alloy (without fibers) is infiltrated. The composite is solidified under high pressure which prevents formation of porosity due to solidification shrinkage. Figure 26 shows a composite of 2024 aluminum alloy/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (Saffil) prepared in this way. The sintered ceramic fiber preforms are very brittle, therefore, while the composites exhibit excellent high temperature properties, they have relatively poor fracture toughness at room temperature. Work is presently underway to toughen these composites by the incorporation of cylindrical holes in the ceramic preforms prior to liquid infiltration.

### Ceramic Matrix Composites

A variety of techniques are available for incorporating a ceramic, or ceramic plus metal, matrix into a 3-D reinforcing preform, and at the same time, producing a new phase between the matrix and the reinforcement that controls the interfacial strength thus the fracture behavior of the composites. Current methods include; infiltration with a low pressure gas (CVI), and a liquid with and without gas reaction. A new method has also been recently developed (Lange) to incorporate a powder, packed at high density, into a preform using pressure filtration. In this workshop emphasis was placed on liquid metal infiltration coupled to metal/gas reaction, (Lanxide™ process), liquid metal infiltration into



Figure 25. TiAl matrix composite fraction surface showing a weak bond between the whiskers and the matrix.

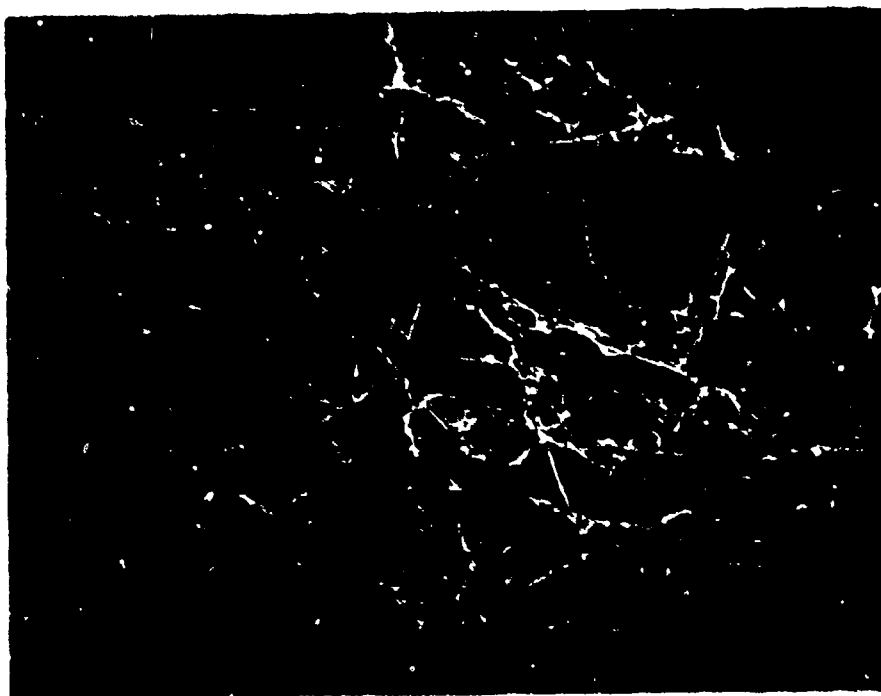


Figure 26. Sintered ceramic fiber preform (15 Vol%  $\text{Al}_2\text{O}_3$  Saffil) liquid infiltrated with 2124 aluminum alloy using a modified version of the process shown in Figure 20. (a) shows an SEM micrograph of the preform at 200x. (b) is an optical photomicrograph of the composite at 400x (from Mehrabian).

dense presintered ceramics (Aksay), and the new colloidal method (Lange). The vapor phase decomposition technique (CVI) was not discussed.

(i) Liquid metal/gas reaction - the Lanxide™ process

The Lanxide™ method is a new technology for the fabrication of ceramic matrix composites (Urquhart). In brief, the method involves the formation of a continuous, dense matrix around ceramic materials (i.e., fibers, whiskers, or particles) using a rapid directed oxidation reaction of a molten metal and a gaseous oxidant. Figure 27 shows a schematic of the process. Growth of the matrix material (a mixture of ceramic oxidation product and unreacted metal) occurs outward from the original metal surface. Transport of the liquid metal to the reaction surface is by creeping flow through microscopic channels in the reaction product. The resulting matrix is predominantly an interconnected ceramic reaction product of the metal and the oxidant. In addition, the matrix also contains some partially interconnected residual metal (typically 5 to 30 percent of the matrix volume depending on reaction conditions).

The growth rate is determined by the rate of oxide formation at the metal/oxidant interface. It is relatively rapid, ~2.5 to 3.8cm in 24 hours for  $\text{Al}_2\text{O}_3$  growth in air, when compared to chemical vapor infiltration (CVI) which is at least an order of magnitude slower. The process occurs only over specific temperature ranges, typically 800 to 1350°C for the  $\text{Al}_2\text{O}_3/\text{Al}$  system. Additional elements (dopants) must be present. Examples include Mg combined with a Group IVA elements such as Si, Ge, Sn or Pb.

The additions may be made to the melt, e.g., in the form of an Al-Mg-Si alloy, or they may be externally introduced as oxides, e.g.,  $\text{MgO} + \text{SiO}_2$ . The resulting microstructures/properties of the matrix are thus dependent on dopants, and time and temperature of fabrication.

The Lanxide™ process has been extended to a number of matrix systems; those described to date include;  $\text{Al}_2\text{O}_3/\text{Al}$ ,  $\text{AlN}/\text{Al}$ ,  $\text{TiN}/\text{Ti}$  and  $\text{ZrN}/\text{Zr}$ . Composites

## COMPOSITE FORMATION

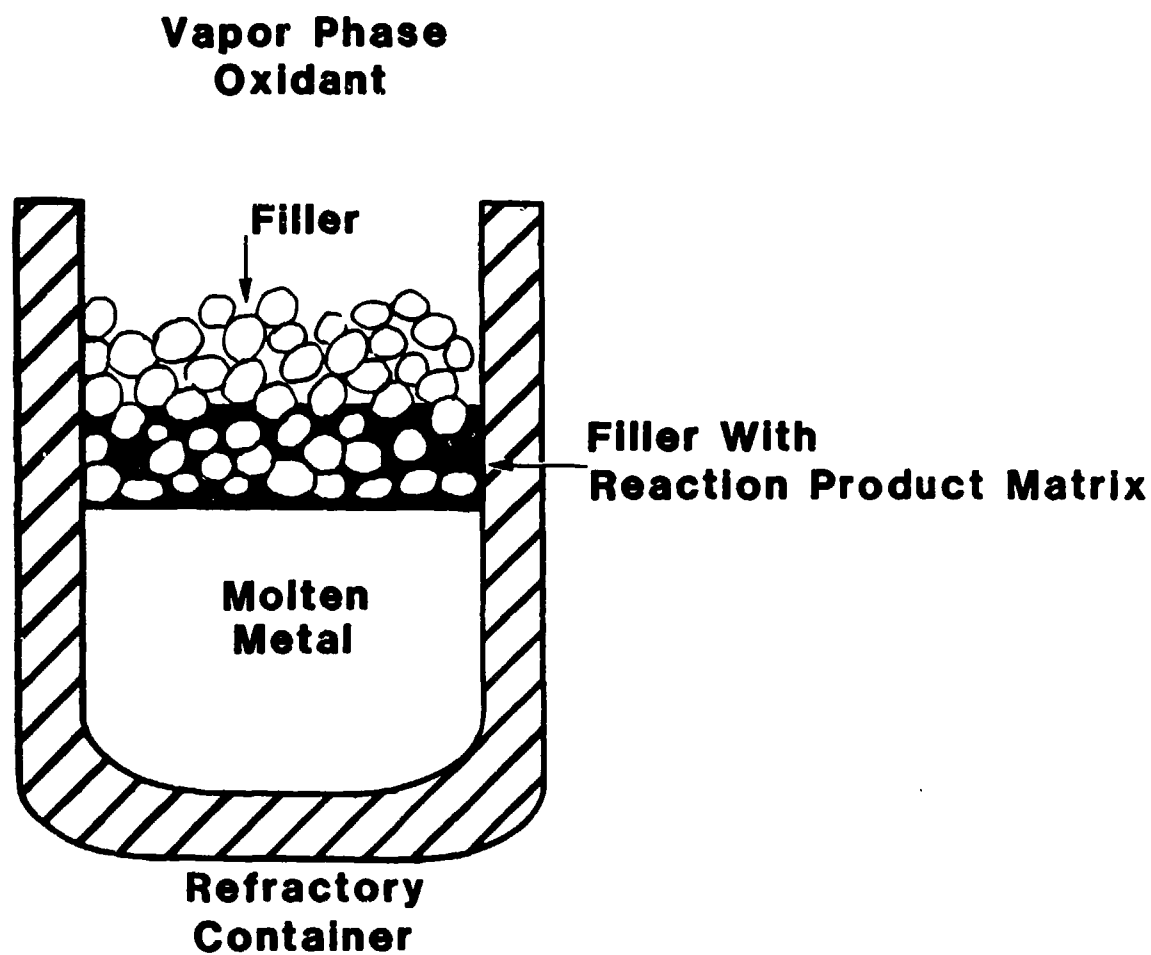


Figure 27. Schematic of the Lanxide™ process (from Urquhart).

described include fillers of  $\text{Al}_2\text{O}_3$ ,  $\text{SiC}$ ,  $\text{ZrO}_2$ , and  $\text{BaTiO}_3$  incorporated in an  $\text{Al}_2\text{O}_3/\text{Al}$  matrix;  $\text{AlN}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{B}_4\text{C}$  and  $\text{TiB}_2$  in  $\text{AlN}/\text{Al}$  matrix,  $\text{TiN}$ ,  $\text{TiB}_2$ , and  $\text{Al}_2\text{O}_3$  in  $\text{TiN}/\text{Ti}$  matrix; and  $\text{ZrN}$  and  $\text{ZrB}_2$  in  $\text{ZrN}/\text{Zr}$  matrix.

Figures 28 and 29 show composites made by the Lanxide™ process containing  $\text{SiC}$  particulate and fiber fillers, respectively, with an  $\text{Al}_2\text{O}_3/\text{Al}$  matrix. The composite in Figure 29 is made of coated Nicalon®  $\text{SiC}$  fiber. Room temperature strength of a composite containing 24 vol% fibers was 785 MPa. The composite retained a strength of 220MPa at 1200°C. Measured room temperature fracture toughness of a lower fiber content composite, 11 vol% fibers, was 18MPa $\sqrt{\text{m}}$ . The fracture surface of this composite is shown in Figure 3. As previously noted, the improved toughness is probably associated with the fiber pull-out shown in this photo micrograph.

The Lanxide™ process lends itself to the production of a variety of shapes, Figure 30, and sizes, up to 20 cm in thickness to date. It should lend itself to production of a variety of optimized microstructures, possibly graded microstructures, which could include ceramic matrices, toughening metallic phases, and appropriately coated fillers (platelets, whiskers and fibers) to form a weak interfacial bond with the matrix.

(ii) Liquid metal infiltration into a dense preforms

Ceramic composites with a fine metallic dispersion can be produced by liquid phase infiltration of dense ceramic preforms (Aksay). The process is essentially identical to that described earlier (Mehrabian) except the preform is significantly denser, its structure is carefully controlled, and wetting conditions are pre-established for low pressure (capillarity assisted) infiltration.  $\text{B}_4\text{C}$  preforms have been consolidated using colloidal techniques to obtain 50 to 70% packing densities. Subsequent heat treatment at  $>2000^\circ\text{C}$  in a graphite furnace result in an interconnected network. Infiltration of aluminum and aluminum alloys into the  $\text{B}_4\text{C}$  network was carried out at  $1180^\circ\text{C}$ . The flexural strength (4-point bending) and Knoop hardness values of the composites are shown in Figure 31.



Figure 28. Microstructure of an Al<sub>2</sub>O<sub>3</sub>/Al matrix composite containing SiC particles produced by the Lanxide<sup>™</sup> process (from Urquhart).

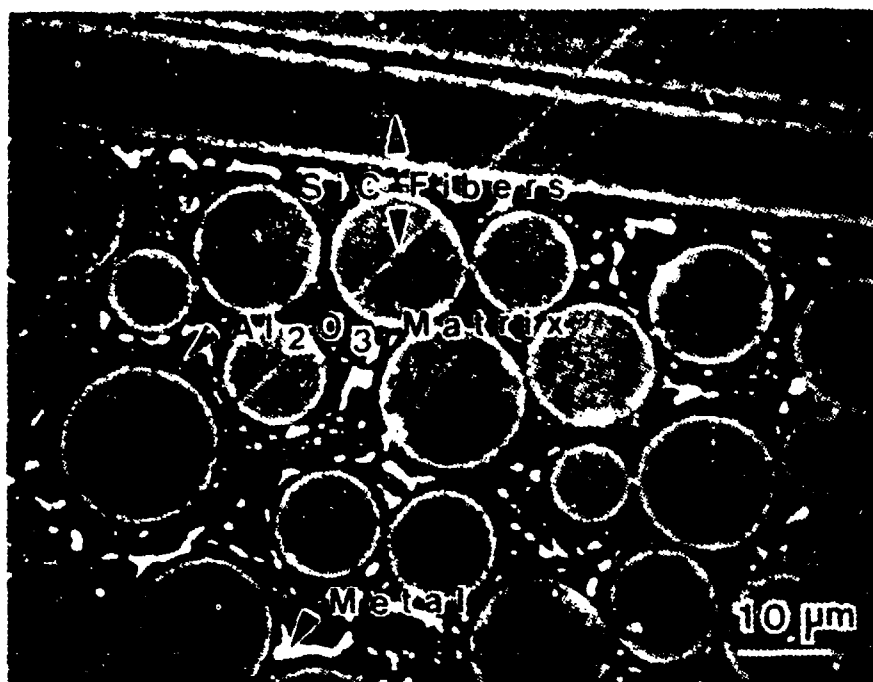


Figure 29. Microstructure of an  $\text{Al}_2\text{O}_3/\text{Al}$  matrix composite containing coated Nicalon<sup>®</sup> SiC fibers produced by the Lanxide<sup>™</sup> process (from Urquhart).

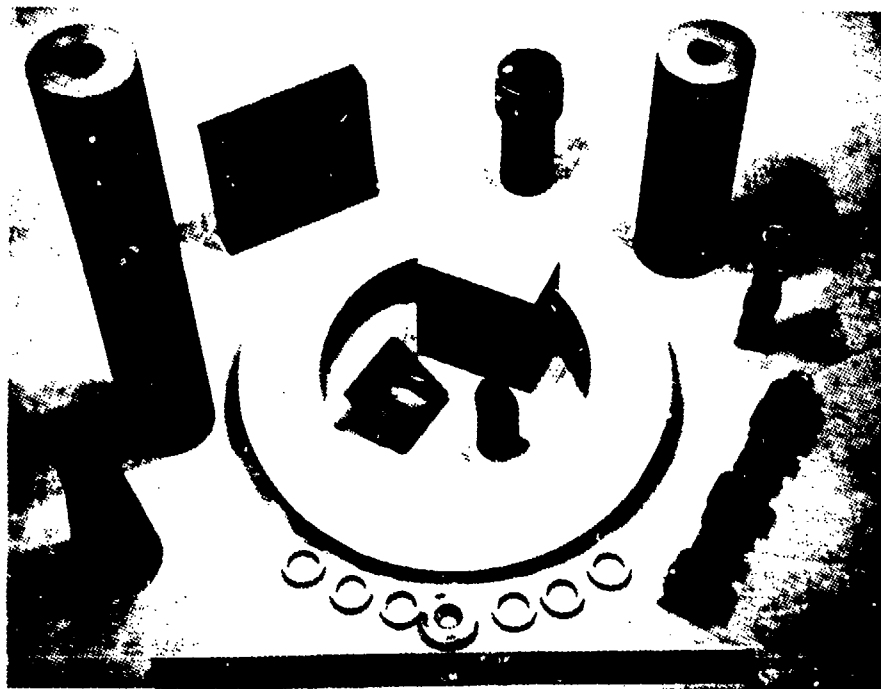


Figure 30. Different ceramic matrix composite shapes produced by the Lanxide™ process (from Urquhart).

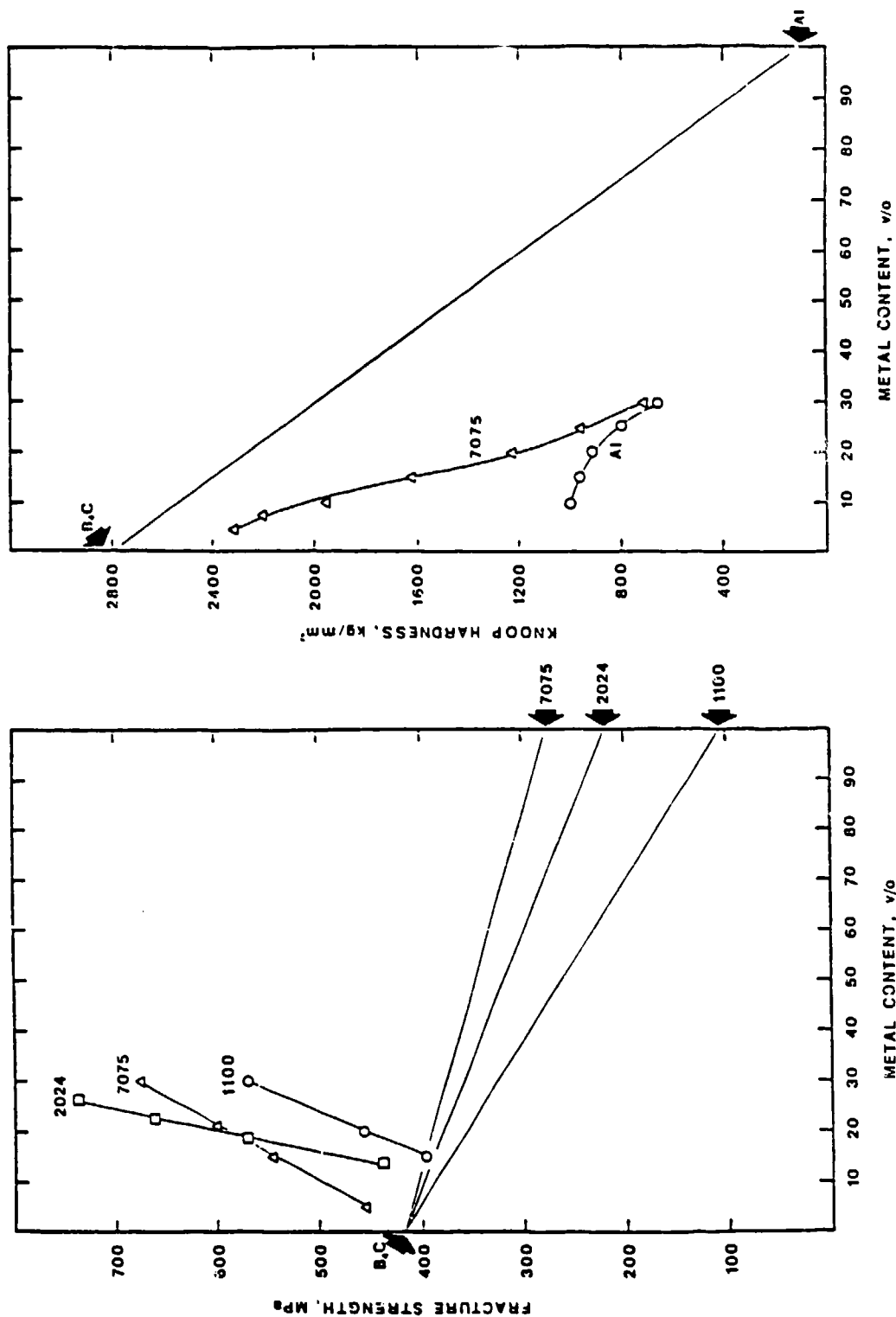


Figure 31. Flexural strength (4-point bending) and Knoop hardness values of B<sub>4</sub>C/Al composites with 1100, 2024 and 7075 aluminum alloys (Aksay).

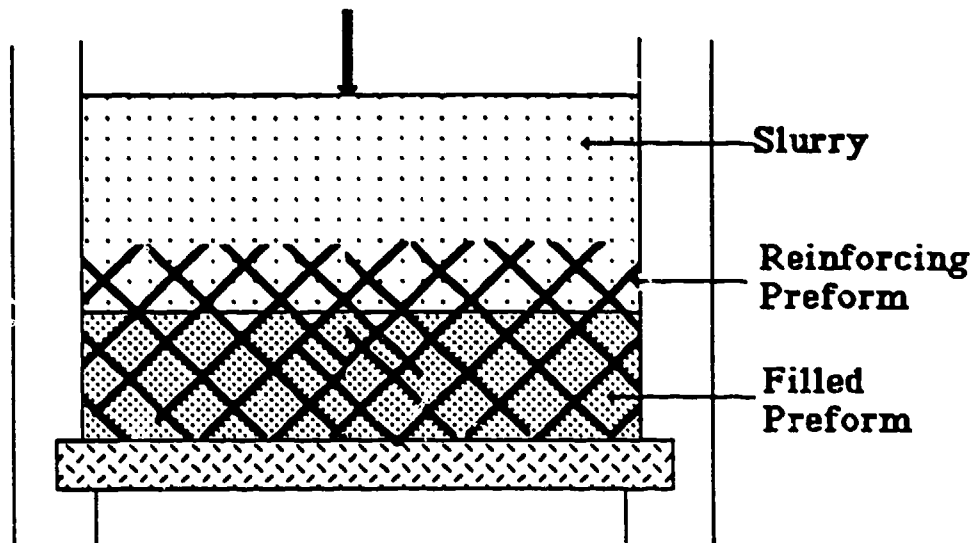
Success of this technique is critically dependent on (i) the wetting behavior of the ceramic phase by the metal, and (ii) the chemical reactivity of the system. For example, 18 phases have been observed in the Al-B-C system. Whereas the highest fracture toughness and strength values were observed (Askay) when the  $Al_4BC$  phase formed as a reaction product.

### (iii) Colloidal techniques

In this method particles are dispersed in a fluid with a surfactant that controls the interparticle forces pack together to form a consolidated layer when the fluid is forced through a filter, Figure 32 (Lange). It has been shown that such a consolidated layer can be formed within a 3-D reinforcing ceramic preform (e.g., woven fiber or felted whisker network) when the particles are not attracted to the preform material and the particles are much smaller than the flow channels within the preform. Colloidal forces are used to manipulate the forces between the particles and between the preform material and the particles. In both cases, these forces must be repulsive.

Colloidal methods combined with sedimentation are first used to fractionate the powder to obtain particle sizes which can flow through the preform. This is followed by the pressure filtration technique shown in Figure 32. The microstructure of a 20 vol%  $Al_2O_3$  Saffil network, such as the one shown in Figure 26(a), infiltrated with 0.5  $\mu m$  particles of  $Al_2O_3$  is shown in Figure 33. Another system currently under study is the  $Si_3N_4/SiC$  with and without BN surface treatments of the SiC fiber preforms.

## Pressure Filtration Applied to Composites



- No Pressure Differential Across Preform
- Demonstrated for  $\text{Al}_2\text{O}_3$  Preform /  $\text{Al}_2\text{O}_3$  Powder
- Appears Useful for Many Composite Systems

Figure 32. Ceramic matrix compositing technique utilizing a colloidal approach coupled to pressure filtration (from Lange).

**20v% Saffil network infiltrated with  $\text{Al}_2\text{O}_3$**

Matrix density ~ 65v%

Fiber diameter: 3 - 5  $\mu\text{m}$

Particle size: ~ 0.5  $\mu\text{m}$

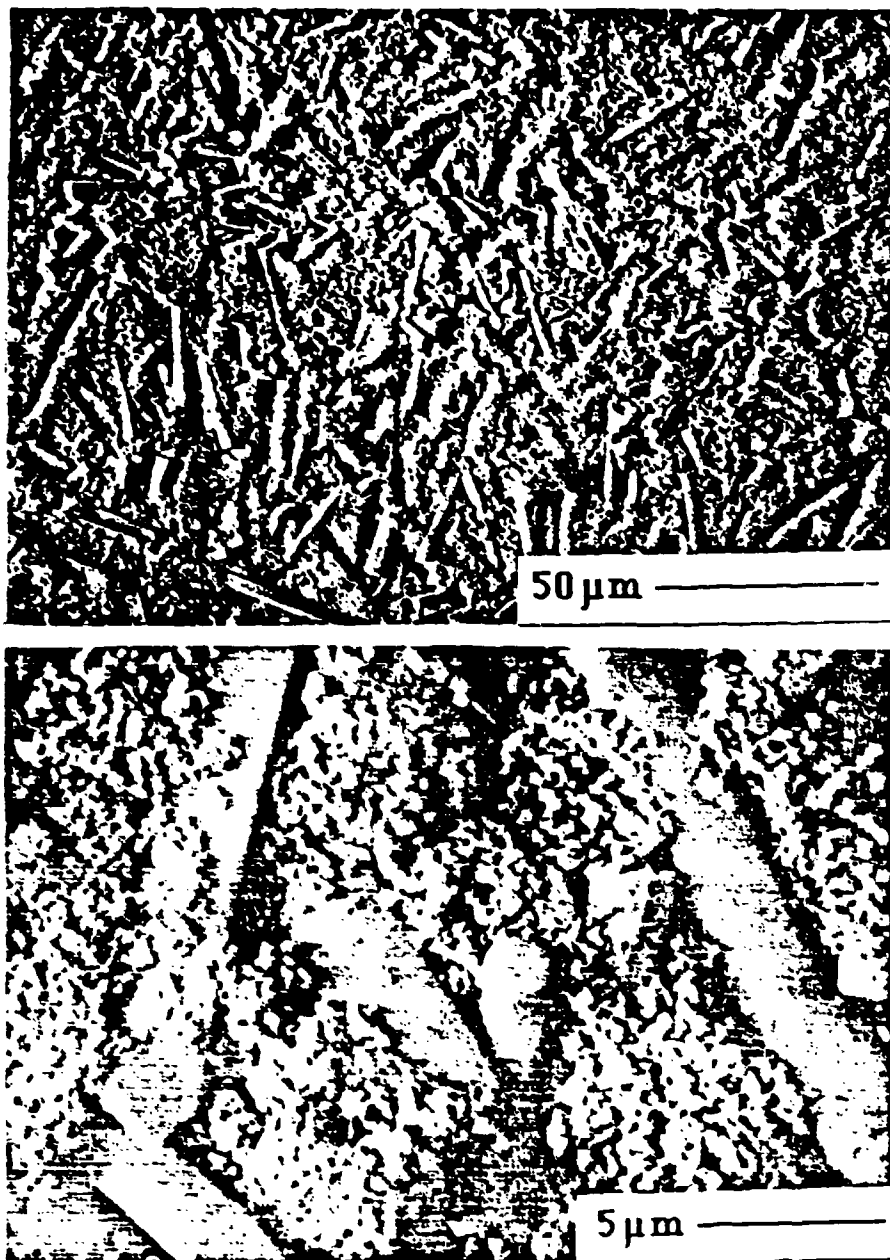


Figure 33. Microstructure of composite prepared by colloidal infiltration (Lange).

## FIBER COATINGS

Coated fibers hold one of the keys to tailoring the strength of the interface which separates the fiber and the matrix. There are numerous issues which bear on this subject including the following:

- fiber/matrix wettability
- coefficient of thermal expansion of fiber, matrix & coating
- chemical compatibility of the coating with the fiber and the matrix
- mechanical properties of the coating
- method of application of the coating.

The implications of tailored properties of the interfaces in composites are enormous. For example, a moderately weak interface can deflect cracks, give rise to fiber pullout and can improve toughness. If the interface is too weak the loads are not effectively transferred to the fibers and both the strength and stiffness of the composite are degraded. For high temperature composites there is the additional requirement that the fiber and coating and/or the matrix and coating be chemically compatible, or if incompatible, have a low rate of reaction relative to the anticipated service life. The compatibility can be determined by thermochemistry, but the kinetics of degradation of incompatible systems are probably more amenable to experiment than to analysis.

The capability for coating fibers has increased and a number of processes are now available at least on an experimental scale. The desired characteristics of an attractive process are shown in Table 3. Whereas Table 4 shows the available processes and their performance with regard to each of these characteristics. It is clear that the capability to coat fibers presently exists on an experimental basis. The real need is to identify some promising fiber, coating, matrix combinations and begin to scope the feasibility and cost of scaling these up to commercially interesting quantities.

**TABLE 3**

**FIBER COATING PROCESS REQUIREMENTS**

- **MINIMAL FIBER DEGRADATION**
  - **UNIFORM THIN COATING**
  - **GOOD "THROWING POWER"**
  - **MINIMAL "BRIDGING"**
  - **GOOD CONTROL OF CHEMICAL PURITY**
  - **SCALABLE TO HIGH THRUPUTS**
- (NOTE: TIGHT PROCESS CONTROL IS REQUIRED)**

**TABLE 4**  
**AVAILABLE FIBER COATING PROCESS**

PROCESS	MATERIALS				CHARACTERISTICS		
	METALS	OXIDES	SULFIDES	CARBIDES/ NITRIDES	THROWING POWER	POTENTIAL FOR BRIDGING	PROCESS COMPLEXITY
CVD	✓		✓	✓	M	L	M
PA-CVD	✓		✓	✓	H	L	L
ION PLATING	✓	✓	✓	✓	H	L	M
PVD	✓	✓		✓	L	H	H
SOL GEL COATING		✓	?		M	H	L
SLURRY COATING				✓	M	M	L

H = HIGH

M = MEDIUM

L = LOW

THE PROCESS MUST BE TAILORED TO THE MATERIAL AND THE REQUIREMENTS

## RECENT ADVANCES IN FIBERS AND COATINGS

The following outlines some comments on recent advances in fibers and coatings. Although significant progress has recently been made in the U.S. with the synthesis of ceramic fibers, the leadership in this field is clearly in Japan.

### New Method for Ceramic Fiber Synthesis

One new method developed in the U.S. for the synthesis of ceramic films was mentioned briefly in the workshop and bears further comment because of its generality. The process starts with a carbon fiber which is then intercalated with a metal chloride such as  $\text{AlCl}_3$ . The intercalated fiber is then burned in air to form a metal oxide fiber according to the reaction:



By varying the oxidation conditions, fibers with different crystalline ordering ( $\gamma\text{-Al}_2\text{O}_3$  and  $\alpha\text{-Al}_2\text{O}_3$ ) and different microstructures (hollow, porous) have been prepared. Also by varying the intercalate species, different ceramic fibers have been synthesized in oxide form ( $\text{ZnO}$ ,  $\text{HfO}_2$ ), including mixed oxides ( $\alpha\text{-Al}_2\text{O}_3\text{:Fe}_2\text{O}_3$ ).

### Electromagnetic Interface Shielding

One applications area for highly conducting fibers is for electromagnetic interference (EMI) shielding. For this application a signal attenuation of 40 dB is required. This can be achieved by densely packed nickel-coated fibers in an epoxy composite, and commercial products based on this concept are currently available. Another approach being developed in Japan (and close to commercialization) is the use of bromine-intercalated vapor grown fibers in a composite material. This approach has promise for relatively low cost shielding material because of the use of as-grown thin CVD carbon filaments for the intercalation process.

### Superconducting Coatings

Continuous carbon fibers coated with NbN have several very attractive properties for superconducting magnet wire applications: the ability to withstand high stresses produced by high currents and fields; ease of preparation and handling, so that coils can be wound easily and cheaply; the ability to withstand thermal and field cycling. Considerable effort has already gone into improving processing procedures for the NbN coated fibers to raise the effective upper critical field  $H_{C2}$  values that can be reached. At the workshop we heard about successful efforts at GA Technologies in fabricating carbon fibers coated with high  $T_c$  superconductors such as  $YBa_2Cu_3O_7$ . Similar work is on-going at a number of other laboratories in the U.S. and elsewhere. There are, however, good reasons to expect significant advances in this area within a very short time frame. Developing composites based on these high  $T_c$  coated fibers will be a logical next step.

One interesting recent development in the fiber technology/coating area is the synthesis of a fiber coating with desired properties on a fiber substrate available commercially in continuous lengths. In principle, this process is similar to CVD epitaxial fiber growth. The motivation for this development is the practical exploitation of the high electrical conductivity of intercalated fibers. Use of the highest conductivity fibers has been limited because they cannot be fabricated in continuous lengths. On the other hand, fibers that can be prepared in continuous lengths do not have high enough conductivities to be of interest for applications, even though their conductivities can be increased by an order of magnitude by intercalation.

Recently, some Japanese workers have developed a continuous fiber which combines the advantages of the continuous ex-pitch fibers with the advantages of the high degree of structural perfection that can be achieved with vapor grown filaments. In this process, highly conductive fibers ( $r = 55 \mu\Omega \text{ cm}$ ) are prepared, starting with a

continuous ex-polymer carbon fiber substrate and epitaxially growing a carbon coating on this fiber substrate by pyrolysis of cyanoacetylene and subsequent heat treatment. The epitaxial coating thus obtained is similar to the vapor phase growth for the thickening process in vapor phase fibers. The structural and transport properties of the fibers thus produced are comparable to the most graphitic filaments prepared by CVD. Furthermore, these fibers have been successfully intercalated to reduce their resistivities by an order or magnitude. Though at an early stage of development, these epitaxially grown continuous fibers offer many attractive features for electronic applications.

CRACK FRONTS TRAPPED BY ARRAYS OF OBSTACLES:  
SOLUTIONS BASED ON LINEAR PERTURBATION THEORY

J. R. Rice

ABSTRACT

What is the configuration of the front of a planar crack which is trapped against forward advance by contact with an array of obstacles? The problem is important to the micromechanics of crack advance in brittle, locally heterogeneous solids. A first analysis, of limited validity, is presented here. It is based on a linearized first-order perturbation solution, derived from three-dimensional elasticity, for the stress intensity factor distribution along the front of a half-plane crack when the location of that front differs moderately from a straight line. A general solution procedure is outlined within that framework, analogies to two-dimensional plane stress crack models of elastic and D-B-C-S elastic-plastic type are cited, and specific solutions are given for crack fronts in contact with a periodic array of blocking obstacles.

## INTRODUCTION

Some elementary modeling is presented of the configuration of the front of a planar crack which is trapped against forward advance by contact with an array of obstacles. The problem is important for the micromechanics of crack advance through brittle, locally heterogeneous materials. The present analysis assumes homogeneous linear elastic material response and also that the obstacle spacing is much smaller than overall crack size. The partial penetration of the crack front between obstacles, and the amplification of the stress intensity factor along regions of contact of the crack front with the blocking obstacles, are evaluated by linear first order perturbation theory (Rice, 1985) for a half-plane crack whose front differs only moderately from a straight line. A detailed solution is presented for a periodic array of blocking obstacles. Unfortunately, the solutions are of limited validity due to their origin in the linear perturbation theory, and they do not suffice, e.g., to address the unstable joining of neighboring crack segments penetrating between obstacles.

## BACKGROUND

First some results from Rice (1985) are reviewed, to allow their later application to some crack trapping problems.

Consider a planar crack in a linear, isotropic elastic solid. The solid is subjected to tensile loadings which would induce stress intensity factor  $K^\circ$  along the crack front if that crack front was straight. For example, when the crack lies on the plane  $y=0$ , grows in the direction of increasing  $x$ , and has a straight tip along  $x=a_0$  (Fig. 1a), we write

$$K = K^\circ[z; a_0] \quad (1)$$

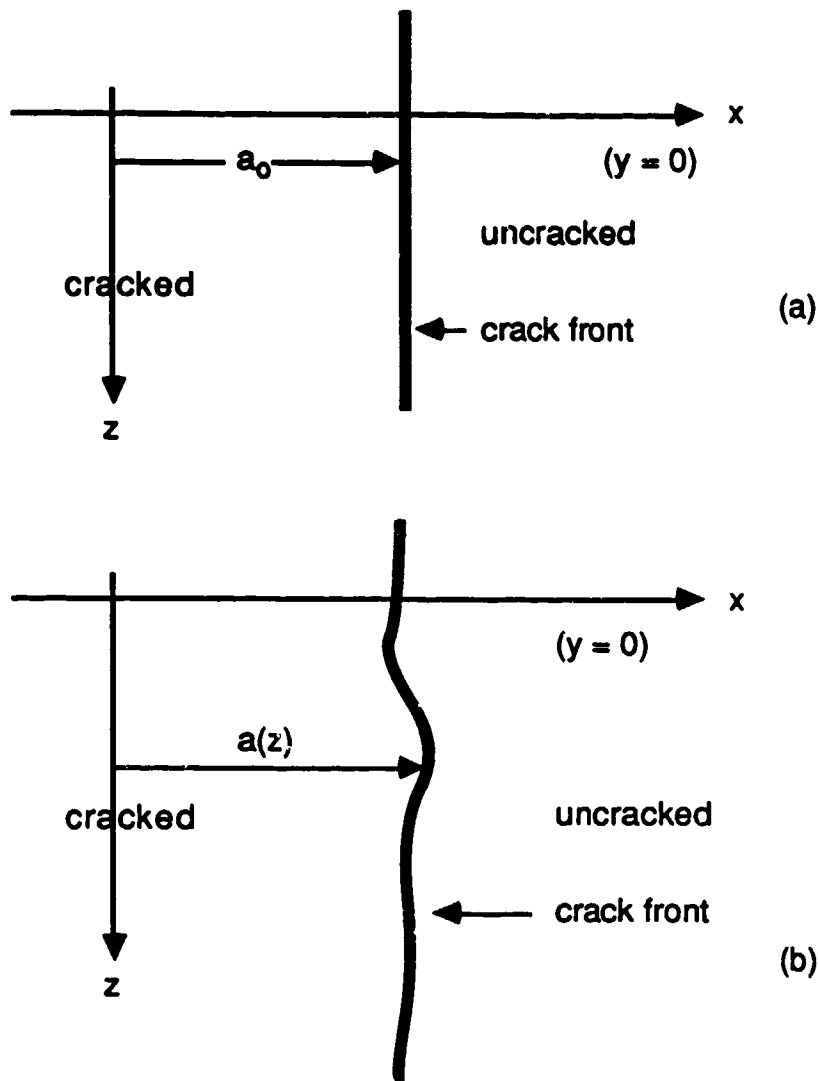


Figure 1.

for fixed applied loadings and, for present purposes, assume that the function  $K^0$  is known. Here the  $z$  axis lies parallel to the straight crack front.

Suppose, now, that the crack tip is not straight, but, rather lies along the arc  $x=a(z)$  in the plane  $y=0$ , as in Fig 1b. The body is subject to the same tensile loadings as before. The function  $a(z)$  will be supposed to fluctuate in  $z$  about a mean value so that, in an average sense, the crack front is still straight. Let  $\lambda$  measure a representative wavelength, along the  $z$  direction, of such fluctuations. It will be assumed that  $\lambda$  is

sufficiently small that the effect of the fluctuations can be modeled as being identical to the effect of the same fluctuations along the tip of a half-plane crack in an infinite solid. Then the solution for the local  $K = K(z)$  at the point along the crack front with coordinates  $(x,y,z)$  equal to  $[a(z),0,z]$  is (Rice, 1985)

$$K(z) = K^0[z;a(z)] + (1/2\pi) PV \int_{CF} K^0[z';a(z)] \frac{[a(z')-a(z)]}{(z'-z)^2} dz' \quad (2)$$

to first order accuracy in the deviation of  $a(z)$  from constancy (i.e., to first order in  $da(z)/dz$ ). Here PV denotes "principal value" and CF denotes crack front.

Now our concern here will be with cases for which the intensity factor along the reference straight crack front varies negligibly with  $z$ , at least over distances of order  $\lambda$ , and also for which the magnitude of  $\lambda \partial K^0 / \partial a_0$  is much smaller than that of  $K^0$ . The latter condition will typically be met if  $\lambda$  is much smaller than overall crack length. Thus, in the cases considered, it will suffice to treat the function  $K^0$  of Eq. (1) as if it was independent of  $z$  and  $a_0$ . That is,  $K^0$  is subsequently regarded as a constant (proportional to the applied loading) which gives the (uniform) intensity factor along a straight crack front and is sensibly independent of crack length over the small excursions to be considered.

Thus Eq. (2) simplifies to

$$\frac{K(z)-K^0}{K^0} = (1/2\pi) PV \int_{-\infty}^{+\infty} \frac{da(z')/dz'}{z'-z} dz' \quad (3)$$

[An integration by parts show that the integral is the same as that with the integrand replaced by  $[a(z')-a(z)]/(z'-z)^2$ ; see Gao and Rice (1986).]

### Formulation of crack trapping and penetration

If we imagine a crack front to be trapped by impenetrable obstacles (Fig. 2a) of some given distribution (and having the same elastic properties as their surroundings), then  $a(z)$  is known along that part of the  $z$  axis where the crack front contacts the obstacles;  $K(z)$  is unknown there. The crack front penetrates between the obstacles, so that on the complementary portion of the  $z$  axis to that just mentioned we may assume that  $K = K_C$ , the critical  $K$  for obstacle-free material. However, along that portion of the axis the penetration depth  $a(z)$  is unknown. In some cases (but not the simple case addressed later here) the border between that part of the crack front in contact with obstacles and that part which penetrates between them is not known a priori (see lower portion of Fig. 2a), and must be determined as part of the solution (e.g., by locating the border such that there is smooth, tangential contact with the crack front).

Thus, if as in Fig. 2a,  $L_{\text{trap}}$  denotes that part of the  $z$  axis along which there is contact with the impenetrable obstacles (trapping) and if  $L_{\text{pen}}$  denotes the complementary part of the  $z$  axis, where there is penetration between obstacles, the conditions  $K = K_C$  in the penetration zone  $L_{\text{pen}}$  and that  $a(z)$  is known in the trap zone  $L_{\text{trap}}$  reduce (3) to the singular integral equation

$$\frac{K^0 - K_C}{K^0} - (1/2\pi) \int_{L_{\text{trap}}} \frac{da(z')/dz'}{z - z'} dz' = (1/2\pi) \text{PV} \int_{L_{\text{pen}}} \frac{da(z')/dz'}{z - z'} \quad (4)$$

for all  $z$  included in  $L_{\text{pen}}$ . Once Eq. (4) is solved for  $a(z)$  along  $L_{\text{pen}}$ , the solution can be inserted into Eq. (3) to solve for  $K(z)$  along  $L_{\text{trap}}$ . Eq. (4) is a standard singular integral equation which is readily solved, all the more so because it also arises in two-dimensional crack theory so that solutions can simply be lifted by analogy from known solutions in that case.

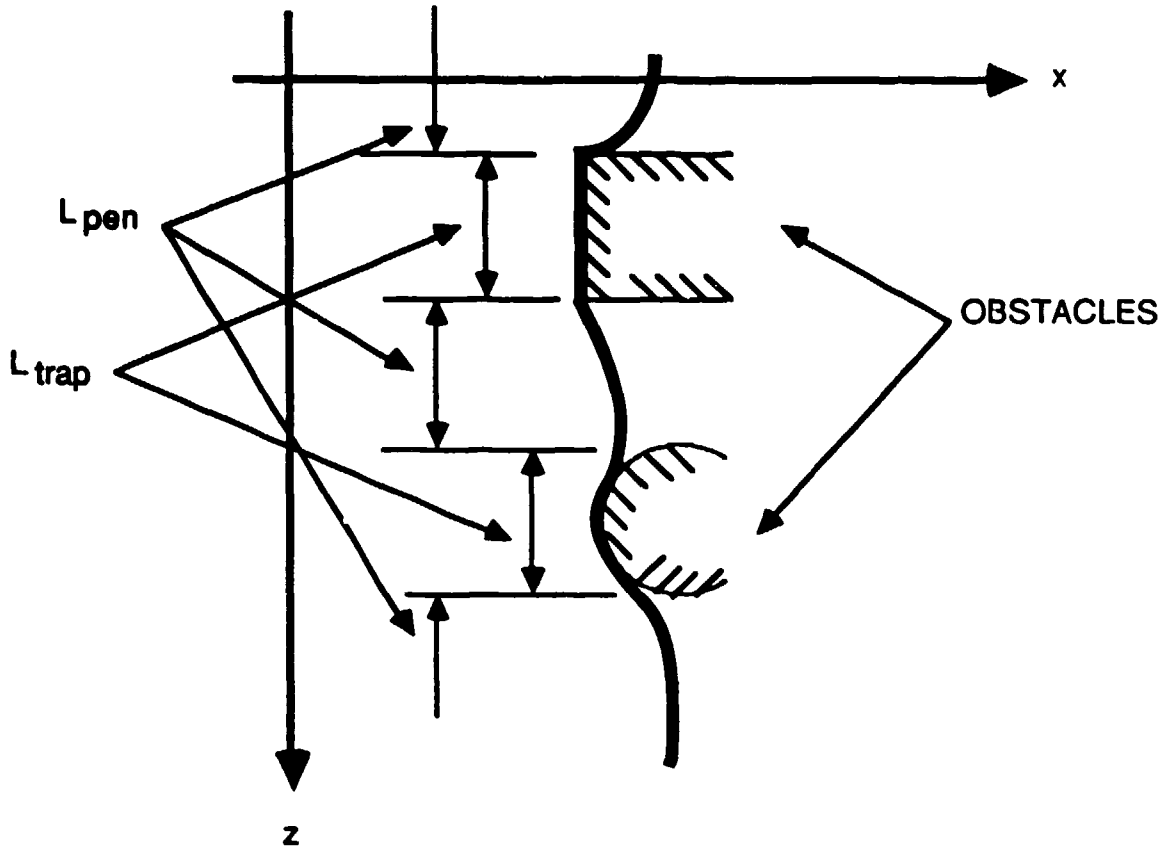


Figure 2a.

#### Analogy to two-dimensional plane stress crack theory

To explore the analogy, consider the two dimensional plane stress of an infinite sheet lying in the  $y,z$  plane, with possible array of cracks or continuous distributions of prismatic opening (edge) dislocations along the  $z$  axis on  $y=0$ . The sheet is loaded by remotely uniform stress  $\sigma_{yy} = \sigma^o$ , and the opening gap (i.e., net  $y$  direction displacement) between  $y=0^+$  and  $y=0^-$  is  $\delta=\delta(z)$ . Thus the stress  $\sigma_{yy}$  along the  $z$  axis, denoted by  $\sigma(z)$ , is the sum of  $\sigma^o$  and the effect of a continuous distribution of dislocations representing the opening gap distribution:

$$\sigma(z) = \sigma^o + \frac{E}{4\pi} PV \int_{-\infty}^{+\infty} \frac{d\delta(z')/dz'}{z'-z} dz' \quad (5)$$

where  $E$  is the elastic tensile modulus. This may be rearranged to coincide exactly with (3) provided that one makes the identification

$$\begin{aligned}\sigma(z)/\sigma^0 &\rightarrow K(z)/K^0 \\ E\delta(z)/2\sigma^0 &\rightarrow a(z)\end{aligned}\tag{6}$$

Thus the 3D problem of a crack trapped by, and partially penetrating between, an array of impenetrable obstacles has the following 2D plane stress analog: The  $z$  axis along the sheet is divided into two parts,  $L_{\text{trap}}$  and  $L_{\text{pen}}$  like in Fig. 2a. Along  $L_{\text{trap}}$  the opening gap is prescribed, i.e., as a given distribution of prismatic opening dislocation corresponding to  $\delta(z) = (2\sigma^0/E)a(z)$ . Along  $L_{\text{pen}}$ , which corresponds to an array of cracks in the sheet, the stress sustained along the crack faces is prescribed as  $\sigma(z) = \sigma^0 K(z)/K^0$ .

Thus known 2D plane stress crack solutions, or new solutions that can be generated by solving the integral equation or, perhaps, by solving an alternate numerical (e.g., finite element) model of the plane stress problem, provide solutions for 3D crack trapping by, and penetration between, obstacles.

The analogy extends further. Suppose that the obstacles are not completely impenetrable, but rather can be penetrated when a sufficiently high  $K$  (say,  $\hat{K}_C$ ) is attained. See Fig. 2b. Then  $L_{\text{trap}}$  reduces, and  $L_{\text{pen}}$  increases, with increase of the "applied" stress intensity  $K^0$ , as the crack front gradually penetrates into the obstacles. Thus  $K(z)$  is non-uniform along  $L_{\text{pen}}$ , being equal to  $K_C (< K^0)$  where the front penetrates between obstacles, and equal to  $\hat{K}_C (> K^0)$  where the front has partially penetrated into an obstacle (e.g., over the segment with length labeled as  $R$  in Fig. 2b). The size of the zones of partial penetration must be determined as part of the solution, and this is done

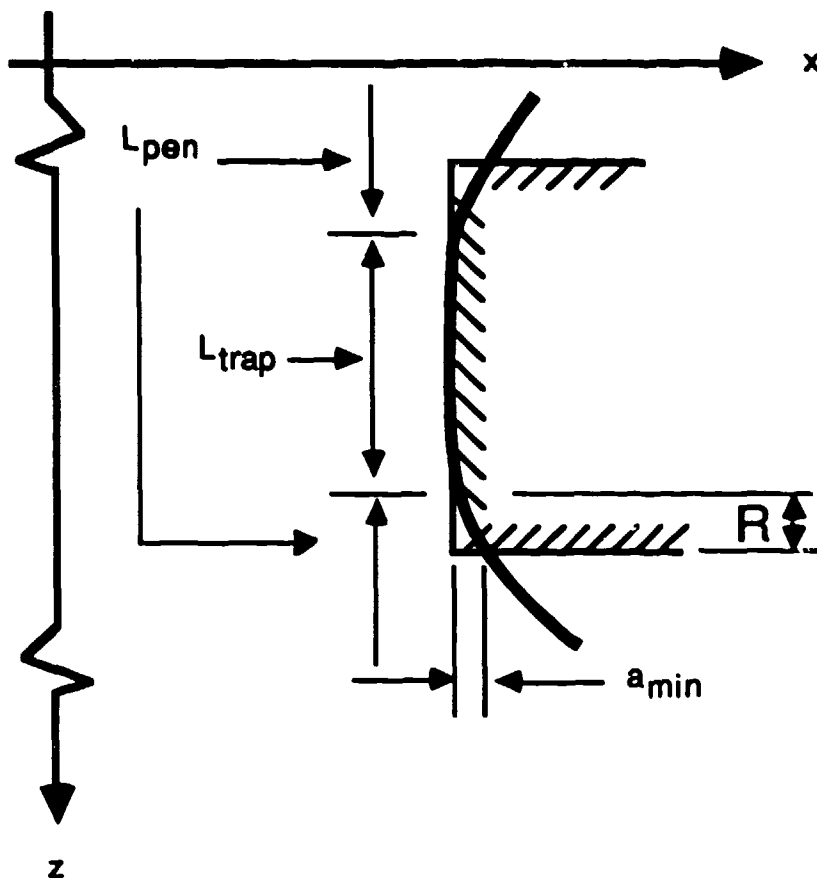


Figure 2b.

by imposing the condition that  $K(z)$  be finite (and, as things must turn out, equal to  $\hat{K}_C$ ) as the border between  $L_{\text{trap}}$  and  $L_{\text{pen}}$  is approached from within  $L_{\text{trap}}$ .

The analogous 2D plane stress problem is then that of an array of cracks in an elastic-plastic sheet whose plastic yielding is described by the Dugdale-Bilby-Cottrell-Swinden procedure. That is, plastic flow is confined to line plastic zones along the  $z$  axis, such that  $\sigma(z) = \hat{\sigma}_C (> \sigma^0)$  along the plastic zones, where the D-B-C-S tensile yield strength  $\hat{\sigma}_C$  is identified as  $\sigma^0 K_C / K^0$ , whereas  $\sigma(z) = \sigma_C (< \sigma^0)$  on the remaining portions of crack face. Thus  $L_{\text{pen}}$  now corresponds to the plane stress cracks and their plastic zones and, of course, the plastic zones correspond to that portion of  $L_{\text{pen}}$  along which

the 3D crack front partially penetrates the obstacles, like the segment of length marked R in Fig. 2b.

Since singular integral representations like in Eq. (3) arise also in describing solutions to the 2D Laplace equation, an alternative formulation of the 3D crack topping and penetration problem is as follows: Let  $\phi = \phi(\hat{y}, z)$  be a 2D harmonic function ( $\partial^2 \phi / \partial \hat{y}^2 + \partial^2 \phi / \partial z^2 = 0$ ) defined in the region  $\hat{y} \geq 0, -\infty < z < +\infty$ . Then  $\partial \phi / \partial \hat{y} \rightarrow 1$  as  $\hat{y}^2 + z^2 \rightarrow \infty$  and the variables  $a(z)$  and  $K(z)$  of interest are given by

$$2\phi(0, z) = a(z), \quad \frac{\partial \phi}{\partial \hat{y}}(0, z) = K(z)/K^0 \quad (7)$$

Thus specifying  $a(z)$  along  $L_{\text{trap}}$  and  $K(z)$  along  $L_{\text{pen}}$  provides mixed boundary conditions on  $\hat{y} = 0$  and the resulting solution of Laplace's equation for  $\phi(\hat{y}, z)$  enables calculation of  $K(z)$  along  $L_{\text{trap}}$  and  $a(z)$  along  $L_{\text{pen}}$ .

#### Periodic array of impenetrable obstacles

Figure 3 shows a periodic array of impenetrable obstacles with center-to-center spacing of  $2L$  and a gap between them, allowing penetration, of  $2H$ . The obstacles have flat edges, parallel to the  $z$  axis, and are aligned so that the crack front encounters them simultaneously. The solution may be developed from the analogy to a 2D plane stress crack problem, using the solution by Koiter (1959) for a periodic array of tensile cracks in plane stress. Alternately, the harmonic function  $\phi(\hat{y}, z)$  may be determined. Thus if  $\zeta = z + i\hat{y}$ , the potential function  $\phi(\hat{y}, z)$  of the last section is given by

$$\frac{\partial \phi}{\partial \hat{y}} + i \frac{\partial \phi}{\partial z} = \frac{K_c}{K^0} + \left(1 - \frac{K_c}{K^0}\right) \frac{\sin(\pi \zeta / 2L)}{[\sin^2(\pi \zeta / 2L) - \sin^2(\pi H / 2L)]^{1/2}} \quad (8)$$

By evaluating  $\partial\phi/\partial \hat{y}$  on  $\hat{y} = 0$ , along  $L_{\text{trap}}$  (e.g., along  $H < |z| < 2L-H$  for the zone centered on the origin in Fig. 3), one obtains from (7) that

$$K(z) = K_C + (K^0 - K_C) \frac{|\sin(\pi z/2L)|}{\sqrt{\sin^2(\pi z/2L) - \sin^2(\pi H/2L)}} \quad (9)$$

This is singular at the borders of the trap zone. The value at the center of a trap (e.g.,  $z = L$ ) is

$$K(L) = K_C + (K^0 - K_C)/\cos(\pi H/2L) \quad (10)$$

and the average value of  $K(z)$  along a trap (e.g., average over  $LH < z < 2L - H$ ) is

$$\bar{K}_{\text{trap}} = (LK^0 - HK_C)/(L-H). \quad (11)$$

To determine the penetration  $a(z)$  from (7) one integrates (8) to obtain  $\phi$  along  $\hat{y} = 0$  ( $\psi = 0$  along  $L_{\text{trap}}$ ), and thus finds that along  $L_{\text{pen}}$  (e.g., along  $-H < z < +H$  for the zone centered on the origin.)

$$a(z) = \frac{4L}{\pi} \left(1 - \frac{K_C}{K^0}\right) \ln \left[ \frac{\cos(\pi z/2L) + \sqrt{\sin^2(\pi H/2L) - \sin^2(\pi z/2L)}}{\cos(\pi H/2L)} \right] \quad (12)$$

Thus the maximum penetration (e.g., at  $z=0$ ) is

$$a_{\text{max}} = \frac{4L}{\pi} \left(1 - \frac{K_C}{K^0}\right) \ln \left[ \frac{1 + \sin(\pi H/2L)}{\cos(\pi H/2L)} \right] \quad (13)$$

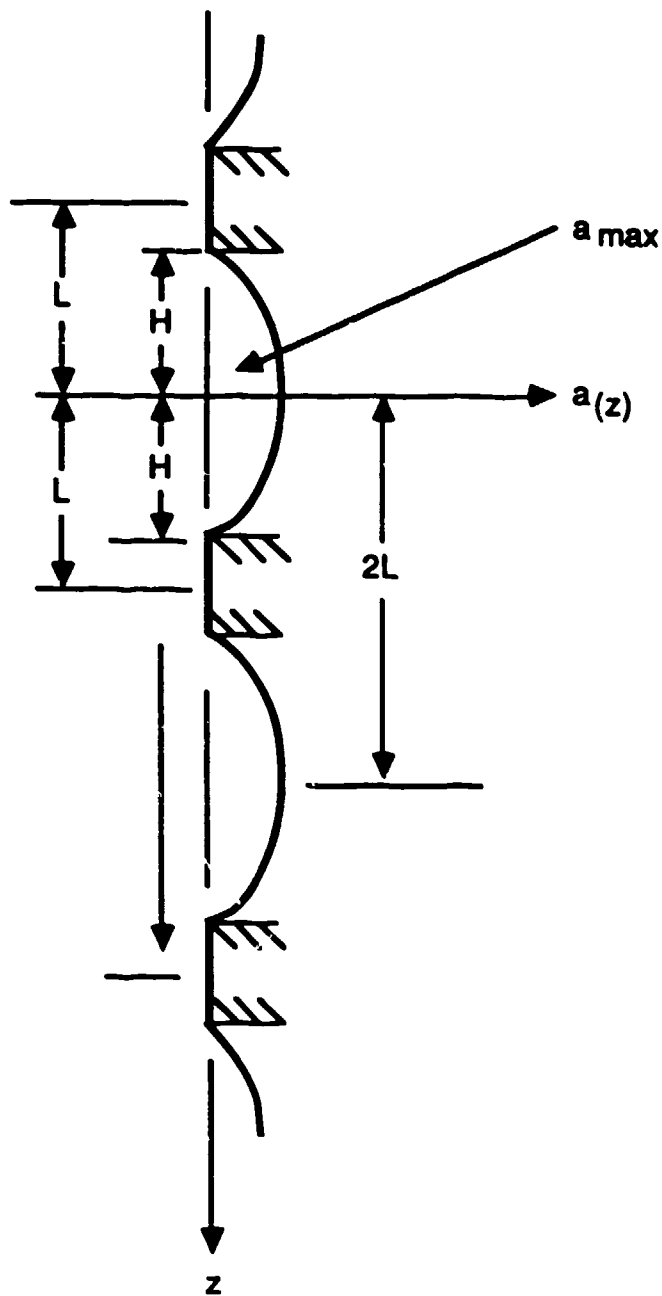


Figure 3.

and the average of  $a(z)$  over a penetration gap (e.g., over  $-H < z < +H$ ) is

$$\bar{a}_{\text{pen}} = \frac{4L^2}{\pi H} \left(1 - \frac{K_C}{K^\circ}\right) \ln \left[ \frac{1}{\cos(\pi H/2L)} \right] \quad (14)$$

Note the  $2H \bar{a}_{\text{pen}}$  is the area swept out by the crack front within each penetration gap.

Table 1 lists the following as a function of  $H/L$ : (i)  $f = (L-H)/L$ , which is the line fraction along the initially straight crack that is in contact with the obstacles; (ii)  $\bar{a}_{\text{pen}}/a_{\text{max}}$ , the ratio of the average to the maximum penetration, which varies from  $\pi/4 (= 0.7854)$  to 1 but is remarkably constant, and rounds off to 0.79 for line fractions above 0.2 and to 0.8 for line fractions above 0.01; (iii) a parameter  $\beta$  which has the following interpretation in terms of the ratio of maximum penetration to the inter-obstacle gap  $2H$ :

$$a_{\text{max}}/2H = \beta(1 - K_C/K^\circ), \quad (15)$$

so that the expression for  $\beta$  can be inferred by comparison of (15) to (13).

Unfortunately the limits to validity of the linearized perturbation expansion are unknown. Rigorously, the equations are valid only when  $(K^\circ - K_C)/K^\circ [= (1 - K_C/K^\circ) \text{ of Eqs. (12) to (15)}]$  is much less than unity. Equivalently, the equations are rigorous for  $a_{\text{max}}/2H \ll 1$ . A clear upper bound to the range of  $a_{\text{max}}/2H$  for which the equations make any sense at all is provided by  $\beta$  of Eq. (15) and Table 1. This is because Eqs. (13, 15) predict that  $K^\circ$  would have to reach infinitely large values to make  $a_{\text{max}}/2H$  reach  $\beta$ , whereas it is clear that sufficiently large (but finite)  $K^\circ$  would cause the bowing crack front segments between obstacles to join with one another, and thus to advance forward as a single crack front whose surfaces are bridged by the unfractured obstacles left behind.

Table 1. Crack penetration between obstacles.

$H/L$	$f = (L-H)/L$	$\bar{a}_{pen}/a_{max}$	$\beta = \frac{a_{max}/2H}{(1-K_C/K^0)}$
0	1	0.7854	1
0.3	0.7	0.7855	1.039
0.5	0.5	0.7864	1.122
0.7	0.3	0.7907	1.298
0.8	0.2	0.7966	1.466
0.9	0.1	0.8108	1.798
0.95	0.05	0.8277	2.169
0.99	0.01	0.8657	3.117
0.999	0.001	0.9040	4.556
1	0	1	$\infty$

Clearly, it is important to deal with such processes, which lie well beyond the scope of the linearized perturbation approach.

#### Gradual penetration of a periodic array of obstacles

Suppose that the periodic array of obstacles in Fig. 3 are not impenetrable but rather, have a finite fracture toughness, say,  $\hat{K}_C$ . Then we use the analogy to the 2D plane stress D-B-C-S model for plasticity at crack tips. The D-B-C-S model for a periodic crack array has been solved by Bilby and Swinden (1965) and Smith (1966) in the case which would correspond to  $K_C = 0$ . It is straightforward to adapt that solution to  $K_C \neq 0$ . The solution is meaningful for the range

$$K_C \leq K^0 \leq (1-H/L) \hat{K}_C + (H/L)K_C, \quad (16)$$

at the upper limit of which the crack front is predicted, within the linear perturbation formulation, to completely penetrate the obstacles (i.e.,  $L_{pen}$  shrinks to zero in Fig. 2b). Of course, the linear perturbation procedures themselves are rigorously valid only for  $K^\circ$  slightly greater than the lower limit  $K_C$ .

Thus, the parameters  $R$  and  $a_{min}$ , as defined in Fig. 2b and characterizing spread of the crack into the obstacle, are given by:

$$R = H \{ (1/\epsilon) \arcsin [\sin \epsilon / \sin \mu] - 1 \}, \quad (17)$$

$$a_{min} = \frac{2H}{\pi} \frac{\sin \alpha}{\epsilon} \int_{\mu}^{\pi/2} \frac{\cos \phi}{(1 - \sin^2 \alpha \sin^2 \phi)^{1/2}} \ln \left[ \frac{\sin (\phi + \mu)}{\sin (\phi - \mu)} \right] d\phi$$

where

$$\mu = \pi(\hat{K}_C - K^\circ)/2 (\hat{K}_C - K_C), \quad (18)$$

$$\epsilon = \pi H/2L, \quad \alpha = \pi(H+R)/2L$$

Observe that  $\mu = \pi/2$  corresponds to the lower limit in (16) and  $\mu = \epsilon$  to the upper limit.

As remarked, the upper limit gives the value of  $K^\circ$  at which the crack front just breaks through the obstacles, at least according to the linear perturbation theory. That limit is

$$K^\circ = K_C + f(\hat{K}_C - K_C) \quad (19)$$

where  $f = (L-H)/L$  is the line fraction of contact.

However the  $K^\circ$  at break-through can be calculated exactly. Observe that with any crack front distribution  $a(z)$  in Fig. 1b, under the conditions assumed here for which the straight-crack-front value  $K^\circ$  of Eq. (1) can be regarded as constant, it is necessary that

$$(K^\circ)^2 = \langle [K(z)]^2 \rangle \quad (20)$$

Here the brackets denote an average, along the entire  $z$  axis, and the equation follows by considering the energy release in a unit translation of the crack front in the  $x$  direction without change of the crack front shape.

Since  $K(z)$  is known everywhere at breakthrough (e.g., as  $K_C$  on  $-H < z < +H$  and as  $\hat{K}_C$  on  $H < z < 2L - H$ ), Eq. (20) gives the exact value of  $K^\circ$  at breakthrough as

$$K^\circ = [K_C^2 + f(\hat{K}_C^2 - K_C^2)]^{1/2} \quad (21)$$

This is seen to agree with Eq. (19) to first order in  $(\hat{K}_C - K_C)$ , as it should.

The ratio of the prediction of (21) for  $K^\circ - K_C$  at breakthrough to the prediction of (19) for  $K^\circ - K_C$  is

$$\frac{(K^\circ - K_C)_{21}}{(K^\circ - K_C)_{19}} = \frac{\sqrt{1 + f(2 + \delta)\delta} - 1}{f\delta} \quad (22)$$

where

$$\delta = (\hat{K}_C - K_C)/K_C \quad (23)$$

Table 2 displays the ratio in Eq. (22) for various  $f$  and  $\delta$  pairs. Clearly, the linear perturbation approach is more appropriate in the range of  $f$  and  $\delta$  for which the ratio is

near unity. The divergence from unity in much of the table emphasizes the necessity of developing analyses that go beyond the linear perturbation approach.

Table 2. Ratio of exact to first order prediction of  $(K^0-K_C)$  at breakthrough.

$\delta$ f	$0^+$	0.5	1	2	4
$0^+$	1	1.25	1.50	2.00	3.00
0.2	1	1.18	1.32	1.53	1.76
0.4	1	1.12	1.21	1.31	1.41
0.6	1	1.08	1.12	1.17	1.22
0.8	1	1.04	1.05	1.08	1.09
$1^-$	1	1	1	1	1

### Acknowledgement

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## AGENDA

### INSTRUMENTATION FOR THE CHARACTERIZATION OF MATERIALS

July 16-17, 1987

#### Objectives

Materials systems can be characterized by a wide variety of methods. Characterization is directed towards relating structure and composition to performance. The purposes of this workshop include consideration of the present state-of-the-art capabilities and identification of opportunities for better methods to enhance sensitivity and resolution of existing methods. Additionally, needs in materials characterization are to be assessed and, hopefully, ideas for new methods will emerge.

#### Thursday, July 16

Introductory Remarks and Introductions - M. S. Wrighton, MRC/MIT

"Use of Ion Beams in Materials Characterization - J. W. Mayer, Cornell

Discussion

"Low Angle X-Ray Reflectography" - P. Pershan, Harvard Univ.

Discussion

"Recent Advances in Surface and Interface Analysis - C. Evans, Evans & Assoc.

Discussion

"Matrix/Fiber Interfaces in Composites: Studies of Single-Fiber Pullout" - L. Drzal, Michigan State

Discussion

#### Friday, July 17

"X-Ray Computer Tomography: Applications to Materials Systems" - J. W. Eberhard, GE

Discussion

"Flash X-ray Tomography" - W. Carter, Los Alamos Nat. Lab.

Discussion

"Solid State NMR Characterization of Materials" - W. A. Ellingson, Argonne Nat. Lab.

Discussion

"Acoustical Methods in Materials Characterization" - B. Khuri-Yakub, Stanford Univ.

Discussion

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**- EXECUTIVE SUMMARY -**

**INSTRUMENTATION FOR THE CHARACTERIZATION OF MATERIALS**

**G.M. Whitesides, M.S. Wrighton, and M.S. Dresselhaus**

**Objectives.** This workshop was organized for several purposes. There now exist many research tools for materials characterization, and one objective of the workshop was to assess the science and technology with the aims of (1) identifying methods that best relate composition and structure to performance and (2) match state-of-the-art methods with practical problems in materials systems. Further, workshop objectives included identification of factors that limit (1) 2- and 3-dimensional resolution, (2) establishment of elemental composition and structure, and (3) applications of research laboratory methods to practical problems in DoD systems. Finally, the workshop was intended to provide suggestions for DARPA action in the area of materials characterization.

**DoD Relevance.** DoD systems demand high performance materials systems that are not necessarily commercially developed for use in the public sector. Also, DoD application scenarios can be uniquely complex and sophisticated. With this general background, state-of-the-art materials characterization has special significance to DoD in connection with new materials development; improvements in the quality and reliability of manufacturing and processing materials systems; performing autopsies on failed systems; and improving maintenance and repair procedures. In each of these areas useful characterization methods can be identified which will ultimately add to military capability.

**Scientific and Technical Summary.** Materials characterization methods can be divided into two classes: (1) surface and interface techniques and (2) bulk and macroscopic techniques. Surface and interface techniques include ones based on

ion scattering (RBS); low angle X-ray reflectivity; ion, electron, or photon excitations (SIMS, Auger, XPS); and microscopy (optical, electron, tunnelling). By using a combination of such methods the elemental compositions can be established ( $\pm 10\%$ ) at a lateral resolution of  $\sim 50$  nm and as a function of depth to several microns with 5nm depth resolution. Atomic level structural resolution on surface can be achieved by microscopy. Elements can be detected at well below 1% of a monolayer on a surface and composition in the ppm range can be done quantitatively by SIMS.

Bulk and macroscopic methods include X-ray tomography (X-ray CT), nuclear magnetic resonance (NMR), flash X-ray tomography, and acoustic methods. These methods are non-destructive methods which can be useful to characterize objects of macroscopic dimensions. X-ray CT can be used to give information regarding inclusions, voids, and wall thickness at  $\sim 50\mu\text{m}$  resolution, based on measures of X-ray attenuation. NMR-CT can be used similarly to study different kinds of materials systems, perhaps best illustrated by medical application, of NMR-CT. Flash X-ray tomography allows studies of systems under load or under operating conditions by providing the time dependence of materials density profiles. Acoustic methods allow characterization of macroscopic objects including systems exposed to liquids such as  $\text{H}_2\text{O}$ .

While new methods and improvements of existing methods are needed, the use of advanced characterization methods are not as widely employed as seems appropriate. Studies, for example, of the surface chemistry of C fibers using surface sensitive probes has been related to the behavior of the mechanical properties of C/epoxy composites. Establishment of relationships between mechanical properties of composites and the structure and composition of the interphase region between filler and matrix represents one significant opportunity, but there are many such areas where use of existing materials characterization will prove useful.

Suggestions for DARPA Action. There are opportunities to foster scientific and technical developments. Significant pay off can be expected from development of (1) high intensity, high energy, reliable X-ray sources; (2) better X-ray and ion array detectors; (3) new and improved techniques to study the interior of solids, especially improving the resolution of X-ray CT, and (4) element specific NMR-CT and imaging, high resolution acoustic methods.

DARPA should encourage the use of existing characterization methods in development of materials systems. In particular, there appear to be many opportunities for study of materials under load or under operating conditions. There is an opportunity to exploit advances in surface/interface methods to understand structural materials.

Technology associated with materials characterization should be transferred to manufacturing and processing, to systems for performance evaluation, and to programs for preventive maintenance and repair assessment. X-ray CT inspection systems are beginning to establish the value of advanced characterization of manufactured parts. More widespread use of characterization methods should be encouraged to improve quality, uniformity, and reliability of military systems.

# INSTRUMENTATION FOR THE CHARACTERIZATION OF MATERIALS

G. M. Whitesides, M. S. Wrighton, and M. S. Dresselhaus

## INTRODUCTION

Methods for characterization of structure and composition of materials and materials systems provide information needed to assess the success of synthesis or fabrication. Such methods may also be useful in assessing performance of materials systems when the relations between composition, structure, and properties are known. A large number of materials systems of DoD interest pose challenging problems in diagnostics. One of the areas of practical interest includes characterization of microelectronic devices where lateral resolution better than  $0.5\mu\text{m}$  is required with sensitivity sufficient to detect unwanted impurities at levels that may be below the part per billion level. In a second area methods are needed to monitor materials systems under dynamic load. A third area involves assessing performance status "in the field" and in characterizing the quality of field repair. Clearly, a wide range of characterization methods are needed to meet DoD's systems needs.

More or less arbitrarily, materials characterization methods can be divided into two broad classes: (1) methods for studying surfaces and near surface interfaces and (2) methods for characterizing the interior of macroscopic objects. Table 1 lists some of the characterization methods that fall into these two categories. A workshop to consider some of the materials characterization methods was held during the Materials Research Council meeting, July 16 and 17, 1987. The following section highlights the "Critical Issues" presented briefly by M. S. Wrighton at the opening of the workshop.

### Critical Issues

While many methods now exist for the characterization of materials, there remain serious shortcomings in applying existing methods to certain kinds of materials

problems. Even with acknowledged deficiencies there are some important areas of opportunity in materials characterization. In discussing various particular methods of characterization the following represent some of the critical issues and questions.

**Table 1. Some Materials Characterization Methods**

**A. Surfaces and Interfaces**

Ion Scattering - Rutherford back scattering (RBS)

Low Angle X-Ray Reflectivity

Electron Scattering - electron energy loss spectroscopy (EELS)

Ion, Electron, Photon Excitation

- Secondary ion mass spectroscopy (SIMS)
- Auger electron spectroscopy (AES)
- X-ray photoelectron spectroscopy (XPS)

Microscopy - optical, electron, tunnelling

**B. Bulk Properties**

Nuclear Magnetic Resonance

X-ray Computer Tomography

Flash X-ray Tomography

Acoustical Methods

- Dimensional Resolution - how can lateral (surface and interface sensitive) and "bulk" techniques be improved with respect to the geometrical resolution? What applications require improvement in geometrical resolution? The problems in materials systems seem to vary widely from the nanometer regime in micro-electronics to measuring wall thickness in the several millimeter regime in monitoring the quality of manufactured parts. The greater than six orders of magnitude spread in required resolution would

seemingly demand the application of a broad spectrum of techniques in characterization. However, in advanced materials systems — from electronics to macroscopic structures --- it seems to always be the case that perceived need for high geometrical resolution instrumentation outstrips existing capabilities.

- Elemental Composition - which methods giving information regarding composition and structure will be useful in establishing relations to systems performance? What new methods can be developed? Chemists working with small molecules where elemental composition and bonding among the constituent atoms is known (or can be known) accurately have made significant progress in understanding the chemical and physical behavior of the small molecules. The problems in solid materials systems are far more complex. For example, does knowing the elemental composition and structure of the surface of a fiber give insight into the behavior of matrix/fiber composites with respect to mechanical properties? In another area, does knowing the composition of an "ohmic" contact to GaAs allow understanding of why it is ohmic and how the complex materials will behave under extremely high current densities? The point is that composition and structure, even when it is known at the atomic/molecular level, is currently inadequate in assessing performance of materials systems.

- Scientific Limitations - what physical limits exist to establishing better geometrical resolution and composition information? What other factors limit developments of new characterization methods and which research laboratory methods should be developed into routine methods? The scanning tunneling microscope (STM) is now a relatively inexpensive and commercially available tool, based on a long known physical phenomenon, that has been transitioned from research to commercialization and routine use in an astonishingly short period of time. What other techniques could be developed based on known physical phenomena? Another important issue concerns whether the

science underlying characterization is being done interactively with technologists facing materials problems.

- "Field" Characterization - which characterization methods can become applicable in assessing the performance status of deployed systems? Another pressing issue of special concern to the DoD is identifying methods most useful in assessing the efficacy of field repair. The problems associated with diagnostics for materials systems actually in use are very complex, and clearly, not all possible methods can be applied. In nuclear power plants corrosion rates of cooling water pipes are monitored indirectly by measuring  $O_2$  concentration with very sensitive, reliable  $O_2$  sensors. This method depends on knowing the relationship between  $O_2$  concentration and corrosion rates. In certain DoD weapons systems sensors for gases, e.g.  $H_2$  in nuclear devices, is a possible way to monitor corrosion, as well. The key is to identify what should be measured and to provide simple low cost, reliable methods for doing it. Identification of methods that would aid in field repair procedures is an important need, but the useful methods technically must also be ones that can be applied considering the difficult logistics and lack of materials characterization expertise among the personnel. Sensors are one form of field characterization, but in many cases monitoring tools based on spectroscopic or tomographic methods will be most appropriate.

- Diagnostics in Manufacturing and Processing - which methods are best suited for on-line materials systems characterization during manufacturing and processing procedures? Use of characterization methods during materials production can improve the quality reliability of finished systems. As in methods applied in the field, only certain methods will be realistically applicable. However, production line use of characterization methods can more realistically involve the user or well-trained personnel and, more importantly, the use of computers to deal with many redundant "decisions."

• DARPA's Role - What opportunities exist for DARPA to qualitatively affect progress in materials characterization that will enhance quality of DoD systems? The several objectives for the workshop on materials characterization include scientific/technological assessment within the context of DARPA's mission. A priori it does not appear reasonable to launch an across the board program to do research and development on new materials characterization ideas. However, such development efforts coupled with major materials problem areas might be opportunities for investment and particularly so if there is the prospect of wider applicability than for the immediate problem. The concluding section of this report conveys the recommendations for DARPA's participation.

#### WORKSHOP SUMMARY

The two-day workshop dealt with only a fraction of the available methods for materials characterization. The subject coverage was limited by time constraints, expertise of members of the Materials Research Council, and the desire to highlight areas of particular interest in connection with identification of opportunities for research, development, and application of materials characterization methods. Broadly, the first day of the workshop concerned methods for characterizing surfaces and interfaces: Rutherford back scattering (RBS); x-ray reflectivity; surface sensitive spectroscopies based on photon, ion, or electron beam excitation; and application of interface sensitive technique to fiber/matrix composites. The second day of the workshop dealt largely with methods for characterizing the interior of materials and materials systems: x-ray tomography, flash x-ray tomography, nuclear magnetic resonance (NMR) tomography, and acoustic microscopy. The following sections highlight some of the accomplishments and issues conveyed in the workshop presentations.

## Surface and Interface Methods.

### • Rutherford Back Scattering - [Invited Speaker: Prof. J. Mayer, Cornell]

Rutherford back scattering (RBS) is a technique stemming from Rutherford's classic experiments concerning  $\text{He}^{2+}$  scattering from Au foil to probe the structure of the atom. The use of RBS as a probe of surfaces had its origin in 1967 --- more than 50 years after the classic experiments of Rutherford. RBS, in most respects, is a technique that has not changed technologically since 1967, except for the use of computer software and hardware to be able to deal rapidly with the data. Basically, the technique is one that gives elemental composition as a function of depth with a lateral resolution that depends on the  $\text{He}^{2+}$  beam spot size. The key is that element identity and amount is established by energy and intensity of backscattered  $\text{He}^{2+}$  ions. The scattering properties of the elements do not depend on the chemical environment, and therefore RBS does not yield information regarding oxidation state or the bonding of the elements. The complexities associated with escape of  $\text{He}^{2+}$  from within a solid require the use of computers for rapid data work-up. Irregularities in surface (roughness) and interfaces (lack of abruptness and irregularities) cause complications in obtaining elemental composition as a function of depth and depth resolution of the order of a few tens of nanometers is the typical best. The same materials realities limit element composition to only about  $\pm 10\%$ . Intrinsic detector sensitivity and the use of only one detector at a particular angle limit the sensitivity of RBS ( $<0.1\%$  of all back scattered ions are typically detected). Detection of an element at 1% within a depth of  $\sim 1\text{-}2\mu\text{m}$  is typically possible. The investigation of interfaces  $1\text{-}2\mu\text{m}$  below the surface is possible. This depth is limited by the energy of the  $\text{He}^{2+}$  ions --- higher energy ions would allow probing of materials at greater depth, but the scattering of  $\text{He}^{2+}$  as function of the ion energy further (and severely) complicates the data analysis. The great advantage of RBS is that within  $\sim 15$  minutes it is possible to

obtain a measure of elemental composition ( $\pm 10\%$ ) as a function of depth, a so-called "depth profile analysis" (down to  $\sim 1\mu\text{m}$ ) for any material.

For routine analysis a commercial system, basically a bench-top system ( $\sim 4 \times 4\text{ft.}$ ), with a small accelerator is available for  $\sim \$350\text{K}$ . A state-of-the-art RBS facility, flexible enough to tackle a broad class of material problems, involves an accelerator of dimension  $\sim 40\text{ft}$  and costing about  $\$1\text{M}$ . A state-of-the-art RBS should be regarded as a "central facility" serving the needs of several research groups. Appropriate maintenance and management at a university should allow use of an RBS by a collection of  $\sim 50$  graduate research students with a significant need for RBS time. Operation on a 24h basis for such facilities is possible.

Two important observations can be made regarding progress with RBS as a materials characterization tool, one social and infrastructural and the other technological. The first point is that advances in the use of RBS can be "forced" by people with the problems stretching the capabilities. More challenging problems will cause needed improvements in the technique, as the research innovations become available in the literature detailing solutions to previously unsolved materials characterization problems. The second point is that technological improvements in detector systems in RBS are needed. The study of polymer systems, for example, by RBS is complicated by the use of large beam current densities that cause materials degradation. More sensitive detectors would allow use of lower beam currents in sensitive materials systems to minimize degradation of materials. At the same time, the elemental sensitivity can be increased with better detectors. Additionally, higher lateral resolution can be achieved, because the better detectors will allow detection of the absolute small number of  $\text{He}^{2+}$  ions backscattered from small areas at incident beam current density that does not degrade the materials. Of secondary technological significance, at least in terms of cost/benefit ratio, would be to do more fundamental work at higher  $\text{He}^{2+}$  energies to

allow composition to be studied at greater depth. The fundamental work involves unravelling the idiosyncrasies of scattering of  $\text{He}^{2+}$  vs.  $\text{He}^{2+}$  energy.

• Low-Angle X-Ray Reflectivity [Invited Speaker: Prof. P. Pershan, Harvard] This technique is applicable to the characterization of a variety of interfaces, including those between condensed phases (solid-solid, solid-liquid) and is one of the few techniques capable of doing so. It can yield sub-nanometer scale structural information perpendicular to the interface in terms of variation in electron density along the axis, but it averages over a large plane of the interface. It is instrumentally highly complex and demanding, and clearly limited to research samples and perhaps a few special systems (e.g., planar mirrors), but in their group of special research samples it yields uniquely detailed information about structurally complex and buried interfaces.

Low-angle X-ray scattering experiments are conducted by reflecting a monochromatic beam of x-rays from a planar surface, and measuring the intensity of the reflected beam as a function of its deviation from the angle of perfect reflectance. The information in this measurement -- the deviation from specular reflectance -- can be interpreted to yield information about the average electron density over the X-ray spot size perpendicular to the plane of the interface, and about certain types of periodic variation in electron density in the plane of the interface. The scale of the variations perpendicular to the interface are commensurate with the wavelength of the X-rays: ~ 0.1 nm.

Because the angle of specular reflection of X-rays from most solids is low (~0.1° from the reflecting plane), it is necessary to have a large area sample with very high planarity. Most work has been carried out with free-standing liquids or films, or with specially polished graphite or silicon flats. The intensity of the reflected X-rays falls off very rapidly with angle, and it is necessary to have an intense source of X-rays and

efficient detectors. Survey experiments can be carried out using rotating anode X-ray sources, but high-resolution work requires access to a synchrotron X-ray light source. Detection is now accomplished using a single point detector. The major technical requirements for improved speed and broader applicability of low-angle X-ray reflectivity are thus:

i.) A broader range of appropriately flat samples. Development of techniques for preparing and maintaining ultra flat samples of a range of metals, semiconductors, ceramics, and liquids, and of layering these materials with micron-scale condensed film of similar flatness at both interfaces, would open a wide range of interfaces to high-resolution structural characterization.

ii.) A recurrent theme throughout the workshop was the utility of X-rays, and new X-ray sources having intensity comparable to a synchrotron light source, but much smaller size, would be very useful. The current engineering development in progress at several electronics firms (NEC, IBM) to contract the construction of "desk top" (~3 -m diameter) synchrotrons to be used as X-ray sources for X-ray microlithography may provide a first step toward such sources, although the wavelength of the devices to be used in microlithography is too large to be useful in low-angle X-ray scattering.

iii.) Detectors are a key element in using the available X-rays efficiently. The single-point detectors now used are intrinsically inefficient, and array detectors with high angular resolution would be more preferable. Given the rapid fall off in intensity as a function of deviation from the angle of maximum intensity of reflection, it is essential that any array detector have very broad dynamic range.

iv.) Analytical methods used in extracting structural data from experimental observations from low-angle X-ray reflection experiments are still relatively primitive, compared with, for example, single-crystal X-ray diffraction. The availability of intense, local, and preferably variable-wavelength X-ray sources, combined with methods of

sample preparation making possible controlled variation in electron density as introduction of anomalous scattering centers should generate more "information rich" data sets and permit the use of more sophisticated methods for data manipulation.

What are the plausible applications of low-angle X-ray scattering to DoD problems? What are the technologies that should be developed to improve this technique? There are a range of model studies involving interfaces (metal-metal, metal-ceramic, ceramic-ceramic, Si/SiO<sub>2</sub>, Si/GaAs, etc) in which the limiting problem is that of sample preparation. It is not yet possible to prepare appropriate samples with acceptable flatness and parallelism. If it were possible to do so, a very wide range of problems relevant to composites, adhesion, corrosion, electronic device fabrication, and mirror fabrication would be possible.

Low angle scattering from multilayer thin film structures offers a technology for X-ray mirrors with high reflectivity. The development of new instruments that would serve as inexpensive, high intensity X-ray sources and array detectors with wide dynamic range would have wide utility.

• Surface and Interface Sensitive Methods Based on Photon, Ion, or Electron Beam Excitation - [Invited Speaker: Dr. C. Evans, C. Evans and Associates, Inc.] Many interface and surface sensitive techniques based on excitation by photons, electrons, or ions are known. RBS involves the use of ions also, but for RBS the scattered incident ions are measured. In the techniques to be described in this section the particles of the incident beam are not typically the particle detected. For example, in X-ray photoelectron spectroscopy (XPS) the number and energy of electrons ejected from surface and near surface atoms are measured while an X-ray beam is used to excite the sample. In secondary ion mass spectroscopy (SIMS) the number and mass of ions ejected from the surface of a sample excited by an ion beam are measured. In this

summary, we will consider only XPS, SIMS, and Auger electron spectroscopy (AES) as techniques based on photon, ion, and electron beam excitation, respectively.

Auger electron spectroscopy (AES) is a very surface-sensitive technique capable of substantially sub-monolayer sensitivity with respect to elemental detectability. Auger electrons, generated by an exciting beam of electrons, from a surface have a kinetic energy characteristic of the elements present. There is some chemical environment sensitivity, but routine use of AES involves determination of composition at high (~ 50nm) lateral resolution. Depth profile analyses can be obtained by combining AES with various "milling" processes. Unlike depth profiling using RBS, AES/depth profile analyses thus involve gross surface chemical processes and the milling chemistry can cause serious problems with respect to interpretation and establishing quantitative measures of elemental composition vs. depth. The lateral resolution of AES, in commercial systems, would appear to be near a physical limit, ~50 nm. The resolution is not limited by inability to focus the exciting  $e^-$  beam, but rather by the fact that the exciting beam is effectively spread by scattering of the electrons beneath the surface of the materials giving rise to Auger electrons from an area much larger than the spot size of the exciting  $e^-$  beam. State-of-the-art Auger spectrometers are available for ~\$400K, including the computer power for 2-D images of elemental compositions. Aside from beam damage, a drawback of AES is that the technique is not applicable to insulating materials.

Like AES, XPS is a technique that has been well-developed and state-of-the-art commercial instruments are available for ~\$400K. Basically, XPS is based on the photoelectric effect where a high energy photon of energy  $E_{h\nu}$  can be used to ionize an atom giving an  $e^-$  having a kinetic energy  $E_{k,e}$  that is given by:

$$E_{k,e} = E_{h\nu} - E_{\text{binding}}$$

where  $E_{\text{binding}}$  is the binding energy of the ejected electron. Since  $E_{\text{binding}}$  depends on the chemical environment, a more "oxidized" element has a higher binding energy, XPS is sometimes referred to as electron spectroscopy for chemical analysis (ESCA). The early promise that XPS would be a routine tool to determine elemental composition and the chemical environment of the elements has not been realized. Nonetheless, XPS takes an important place among methods for surface (and near surface) characterization, because insulating samples can be measured and there is a good deal of chemical information revealed. The lateral resolution is limited at present to about 0.1 mm. Additionally, there is still concern regarding X-ray beam damage. The depth sampled in XPS depends on the  $E_{k.e.}$ -dependent escape distance of the photoejected electron, but in general, the depth sampled is ~2.5nm or greater. The typical sensitivity with respect to surface atoms in XPS is less than for AES which is less than SIMS. However, like AES and SIMS, XPS can be used to detect fractions of a monolayer (albeit for larger surface areas).

SIMS is a very surface sensitive technique (0.5 - 1nm), with the highest sensitivity, and capable of high lateral resolution (~100nm). A major drawback with SIMS stems from difficulties arising from different secondary ion yields for a given element depending on the "matrix" from which the ion emerges. Thus, while SIMS is extremely sensitive, establishing quantitative elemental composition of surfaces requires very careful use of "standards" to calibrate the measurements. One of the exciting advances in SIMS is the use of imaging and profiling, with computer software and graphics, to provide high lateral and depth resolution views of complex interface systems. The technique of imaging/profiling suffers from differences in the milling rate for different materials, but excellent results can be obtained when care is taken to deal with the milling chemistry. Another problem with SIMS stems from difficulties associated with discriminating species having the same nominal mass, e.g., Si, CO, N<sub>2</sub> are all nominally

mass 28 and  $\text{Si}_2^+$  and  $\text{Fe}^+$  are both nominally mass 56. These problems can be solved by measuring exact masses requiring better mass spectrometer detectors, and the state-of-the-art SIMS are commercially available with such capability. Another technique to solve problems of the  $\text{Si}_2^+$  vs.  $\text{Fe}^+$  sort is to use a method to remove molecular ions such as the  $\text{Si}_2^+$ . This experimental approach is not necessarily generally desired, however. Measurement of the exact mass of molecular ions can be essential to understanding the nature of surfaces modified with molecular materials. Such systems would include biosensors, metals coated with molecular monolayers (for lubrication, wetting, adhesion), and electrocatalytic surfaces. The use of SIMS to characterize the surfaces of electronic devices and device materials is well established, but the technique has enormous potential in other areas as well.

A versatile SIMS system, equipped with ~100nm lateral image resolution, exact mass measuring capability, and the several sources needed for studying a variety of material systems costs ~\$900K. Techniques related to SIMS involve mass measurement of laser-ejected ions and recently work has shown that ionization of the "plume" of neutrals species from beam excited surfaces leads to element and matrix independent sensitivities. So-called sputtered neutrals mass spectroscopy (SNMS) offers the prospect of establishing surface elemental composition without expending as much effort in measuring calibrating standards. The SNMS technique is commercially available at ~\$300K, but lacks good lateral resolution and is not as sensitive as SIMS. A summary statement regarding XPS, AES, and SIMS is that good commercial instrumentation exists, albeit each is an expensive analytical/ research tool. Surface analysis of materials requires more than one technique. The capital cost and cost and complexity of maintenance of the instrumentation would suggest that a central facilities mode of operations is best for serving a significant community with diverse materials problems.

• Surface/Interface Characterization and Composite Properties - [Invited Speaker

- Prof. L. Drzal, Michigan State University] The use of surface characterization methods to establish the nature of C fibers treated in various ways can, in principle, contribute to an understanding of the behavior of composites such as C fiber/epoxy composites. "Behavior" refers to mechanical properties. The nature of fiber interaction with a matrix is crucial to understanding the strength of the composite, and arguably the interaction of the fiber with the matrix can be better understood by knowing the chemical functional groups on the surface of the fiber. Indeed, XPS analysis of C fiber surfaces can be correlated with the mechanical properties of a C-fiber/epoxy composite. The crucial experimentation involves studies of the behavior of a macroscopic part of epoxy containing a single fiber. Studies show that fiber/matrix separation vs. matrix cracking after fiber fracture does depend on the chemical pretreatment of the fiber, for example. From such single fiber studies the behavior of an actual composite, containing a large volume fraction of fiber, can be rationalized.

The promising correlations found with various chemical pretreatments leads to the conclusion that an "interphase" between the fiber surface and the matrix is really the crucial region in determining the composite properties. The interphase extends tens of nanometers from the fiber surface. An example of a challenging characterization problem is to image the interphase region of a C fiber coated with non-polymerized epoxy resin in a composite structure. It is not at all clear that existing characterization methods are applicable to actual composites, but the objective of correlating surface and interphase composition with mechanical properties is a significant research goal. This materials problem is of the sort that will cause an expansion of the scope of materials characterization methods.

With regard to instrumentation for characterizing strains in carbon/carbon and other composites, discussion was stimulated at the Instrumentation Workshop on

strain-sensitive interactions in carbon fibers. Such interactions, of course, form the basis for sensitive instruments. In this regard some background on the piezoresistance of carbon fibers is worth noting.

There are several causes for piezoresistance phenomena in carbon fibers. When a fiber is put under uniaxial tension, it will increase in length, and usually decrease in diameter. Both of these geometric effects serve to increase the resistance of the fiber, assuming that the resistivity does not change. One therefore writes the total piezoresistance as:

$$(\Delta R/R) = (\Delta L/L) - (\Delta A/A) + \Delta \rho/\rho$$

where the first two terms on the right hand side of the equation are due to strain-induced geometric effects, while  $\Delta \rho/\rho$  is due to changes in the resistivity itself. Here  $R$  is the measured resistance, while  $\Delta R$  is the change in the resistance per unit strain,  $L$  is the sample length, and  $\Delta L$  is the change in length (so that  $(\Delta L/L)$  is the strain  $\epsilon$ ),  $A$  is the cross sectional area,  $\Delta A$  is the change in  $A$  per unit strain,  $\rho$  is the resistivity and  $\Delta \rho$  is the change in  $\rho$  per unit strain. Normally  $(\Delta L/L)$  and  $(-\Delta A/A)$  are both positive so that  $(\Delta R/R)$  increases due to geometric effects. For highly disordered carbon fibers, the dominant contribution to  $(\Delta R/R)$  is through geometric effects, so that in this case  $(\Delta R/R)$  is small and positive.

For carbon fibers with a moderate degree of ordering, electronic contributions become important, leading to a contribution from the  $(\Delta \rho/\rho)$  term. Here the effect of strain along the length of the fiber, decreases the interlayer separation of the graphite sheets, thereby increasing the interlayer overlap energy, increasing the magnitude of the Fermi level and increasing the carrier density and hence the conductivity. In the regime where scattering processes are dominated by defects, the contribution  $(\Delta \rho/\rho)$  is negative and

can be larger than the geometrical effects, often leading to a larger magnitude for ( $\Delta R/R$ ) than for the disordered fibers, but with a negative sign and a non-linear (often also non-monotonic strain dependence). Finally, when the scattering processes are dominated by phonons in the best-ordered fibers, the strain decreases the carrier mobility. This effect on the mobility can become more important than the increase in carrier density, leading to a large positive ( $\Delta R/R$ ) term.

In the same way, a strain-induced change in the carrier density and carrier mobility should give rise to changes in the optical constants  $n$  and  $k$ , which is the basis for some of the analysis by Drzal of fiber strains arising from bonding of the fibers to the matrix in composite materials.

• Bulk Materials Characterization Tools. X-Ray Computer Tomography. - [Invited Speaker, Dr. J. Eberhard, GE] X-Ray computer tomography (X-ray CT?) is a method for the characterization of materials systems including metal and composite structures. X-ray CT evaluates structural integrity, dimensional integrity, and materials properties including density and certain chemical properties. The technique is one based on measuring the attenuation of the intensity of X-rays, and, since highly X-ray absorbing materials (e.g., heavy metals) are often of interest, there is need to use an intense, high energy X-ray source. X-ray CT currently can be used to give  $\sim 0.25\text{mm}$  spatial resolution for the characterization of materials systems in connection with establishing dimensional and structural integrity. The properties of interest for metals include voids/inclusions, microshrink, and wall thickness/dimensions. For composites the properties of interest include voids/inclusions, low density regions, high density inclusions cracks, delamination, and fiber management. The value of using X-ray CT for systems characterization is that a combination of experience and fracture mechanics will allow the measured properties to be related to systems performance. Thus, X-ray CT

inspection allow improvement in reliability of manufactured parts, and use of X-ray CT inspection in the field would allow assessment of the systems status.

Several commercial X-ray CT inspection systems have been developed for work on DoD-relevant materials system as Table 2 shows. Such systems cost in the \$1-2M range and involve unique designs (largely driven by the particular application) and include customized computer systems. Differences in the technology in the various systems involve sources and detectors. Indeed, the main needs in further developing X-ray CT involves (1) intense, reliable, high energy X-ray sources and (2) improving the detectors and detector electronics.

The ~0.25mm typical resolution of X-ray CT can be pushed to ~50 $\mu$ m, but even this resolution is too low to give detailed insight into many important materials systems such as fiber-based composites. Use of intense X-ray sources such as those available at synchrotron facilities may, in fact, allow 1 $\mu$ m resolution. At such resolution only relatively small volumes can be scanned quickly. However, the 1 $\mu$ m resolution would certainly be useful in better characterizing actual systems at the resolution required to relate the measured properties to performance. The X-ray CT, with the penetrating power of energetic X-rays, certainly provides a valuable tool as it is -- 50 to 250 $\mu$ m resolution, but it seems that many crucial materials shortcomings are not revealed at such low resolution.

Aside from advances in resolution, X-ray CT can be improved with respect to the information provided concerning chemical composition. By using X-ray sources at two (or more) energies it is possible to discriminate different materials based on differences in the attenuation of the X-ray intensities. Such chemical information would clearly enhance the value of the X-ray CT in characterization on materials systems which are "unknowns" with respect to composition. However, the use of multiple energy sources will have the effect of increasing the scan time, unless there are advances in the

**Table 2. State of the Art X-Ray Computed Tomography Inspection Systems \***

**General Electric (GE)**

System - X-Ray Inspection Module (XIM)

Target Part - Turbine Blades

Object Size - 3 in

Spatial Resolution - 0.25 mm

Contrast Resolution - 2%

Source - 420 KVP X-Ray Tube

Detector - Xenon Ionization Chamber & Charge Collection

**Advanced Research and Applications Corp. (ARACOR)**

System - Air Force Advanced Computed Tomography System (AF/ACTS 1 & 2)

Target Part - Rocket Motors and ICBM Nozzle Components

Object Size - 28 in, 92 in

Spatial Resolution - 1 mm

Contrast Resolution - 5%

Source - 420 KVP X-Ray Tube, 15 MeV Linac

Detector - Scintillator and Photo Diode

**American Science and Engineering (AS&E)**

System Rocket Motor Scanner, Mouse Scanner

Target Part - Trident C-4 Rocket Motor, Small Biological Specimens

Object Size - 2m, 2.5cm

Spatial Resolution - 2mm, 0.05mm

Contrast Resolution - 5%, 2%

Source - 15 MeV Linac, 90 keV rotating anode tube

Detector - Scintillator & Photodiode, Patented Scintillator & Photodiode Array

**Bio-Imaging**

System - SCTIS, TAIA

Target Part - Rocket Motors, Artillery Shells

Object Size - 50", ?

Spatial Resolution - 0.5 mm

Contrast Resolution - Several %

Source - 15 MeV Linac, Cobalt 60 Radioisotope

Detector - Solid State Scintillator, Counting Detector

**Scientific Measurement Systems, Inc. (SMS)**

System - Various

Target Part - Automotive Engine Blocks, Turbine Blades, Trees, Concrete, etc.

Object Size - Wide Range

Spatial Resolution - Varied

Contrast Resolution - Varied

Source - 320 KVP Tube, Microfocus Tube, Linac, Radioisotope

Detector - Plastic Scintillators and PM Tubes

\* Information provided by J. Eberhard of GE

detector technologies. It is important to recognize that, as with improving resolution, multiple energy X-ray probing will require development of new sources.

• Nuclear Magnetic Resonance of Solids - [Invited Speaker, Dr. W. Ellingson, Argonne National Laboratory] Nuclear magnetic resonance (NMR) of solids is a technique that can be used to provide information concerning the chemical nature of the solid. For many years, since the early 1960's, chemists have employed NMR for the characterization of molecules dissolved in solution. The technique is an extraordinarily powerful tool in structural characterization of molecule having elements which have a nuclear spin, because the NMR resonances (radio frequency interrogation in the presence of a magnetic field) depend on the local environment. Thus,  $^1\text{H}$ -NMR gives resonances for every chemically distinguishable  $^1\text{H}$  in a molecule. NMR for  $^{2\text{H}}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$ ,  $^{29}\text{Si}$ ,  $^{15}\text{N}$ ,  $^{17}\text{O}$ ,  $^{195}\text{Pt}$ , etc. are now more or less routine for molecules in solution and give chemists detailed insight into the structure of molecular systems. More recently NMR techniques applicable to solids have been developed and commercial spectrometers are now available at a cost of several hundred thousand dollars. The advances needed to probe solids stem from the general lack of sufficient resolution to distinguish chemically distinguishable  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ , etc. Now, in favorable cases, solid state NMR of molecular crystals, molecular polymers, and high surface area inorganic materials can be carried out routinely to give high resolution spectra. The use of solid state NMR will grow dramatically and will provide unprecedented levels of chemical information for solids.

Imaging the interior of macroscopic objects with NMR is a major development (started in the early 1970's) that is now being used in medical diagnostics. NMR tomography for medical application is a technique based on the variation of relaxation times of excited  $^1\text{H}$ - nuclei in  $\text{H}_2\text{O}$  found in different environments. The resolution of

NMR tomographic images is a fraction of a millimeter, and the computer needs are similar to those in X-ray CT. With NMR imaging there is the possibility of gaining chemical specific information by investigating other nuclei such as  $^{13}\text{C}$  or  $^{21}\text{P}$ . The remarkable advances in NMR imaging and the phenomenal rate of practical implementation in medical diagnostics suggests that the NMR imaging would be applicable to the characterization of materials systems. The development of commercial systems for imaging human subjects at a cost of \$1-2M indicates that the technology now exists to characterize the interior of rather large objects.

One immediate application of NMR imaging technology is to the characterization of porous objects. The idea is to fill the pores of the object with a liquid and then to image the NMR-active liquid. This technique can be applied to the characterization of ceramic objects to assess the structural integrity in much the same way the X-ray CT can be used to characterize X-ray absorbing (dense) materials. An important feature in NMR imaging is that the relaxation time of the excited nuclei not be too long. Thus, the investigation of liquid filled objects is analogous to NMR imaging of human subjects.

A technological limitation to NMR imaging of rigid solids in general appears to be a problem associated with long nuclear relaxation. However, this problem can possibly be dealt with as it has been dealt with in solution  $^{13}\text{C}$ -NMR by introducing paramagnetic centers to accelerate the relaxation. Additionally, basic research is now being carried out to determine high resolution NMR at very low temperature ( $< 1\text{ K}$ ). At such temperatures there is the possibility that NMR will be extraordinarily sensitive.

• Flash X-Ray Tomography - [Invited Speaker - Dr. W. Carter, Los Alamos National Laboratory.] Flash X-ray tomography is a technique that can be used to characterize materials systems under dynamic conditions. Basically, the technique allows studies of transient events by using a pulse of X-ray light to probe the system at a

particular time. At Los Alamos studies of the events following detonation of high explosives have been carried out with the goal of obtaining absolute material density distributions within an object undergoing dynamic deformation. The preliminary studies have yielded dramatic images of various objects undergoing deformation following detonation of a high explosive. These images include the materials density in a shaped charge in mid-flight and the density distribution in a high explosive while undergoing detonation. The X-ray pulse can be as short as a few nanoseconds but is typically tens of nanoseconds. The short, intense high energy X-ray pulse allow studies of dense materials systems.

The Los Alamos facility used for flash X-ray tomography is football field size and costs ~\$100M, but can be used by the on-site personnel for some of the unique problems associated with DoD systems. In their work the detector is a film pack which introduces problems not encountered in the X-ray CT, because processing of the film becomes a serious source of variation. Also, the flash technique suffers from variation (flash to flash) in beam profile and intensity. Despite these, and other problems, the Los Alamos work has produced remarkable images. Figure 1 shows, for example, the density profiles for a cylindrically symmetrical object some milliseconds after a detonation of an object where the parent is a disc of constant density. Part of the importance of this work is in validating methods for predicting the density profiles (as a function of time) which are used in designing armor penetrating weapons.

Clearly, flash X-ray tomography as practiced at Los Alamos is not likely to be a common technique in materials characterization. However, the results obtained do show that it is possible to gain information about the interior of materials systems in transient events. The information obtained provides more insight than a normal photograph, because the density of the interior can be measured. There would appear to be many opportunities to apply flash X-ray tomography to systems of DoD importance. Wide

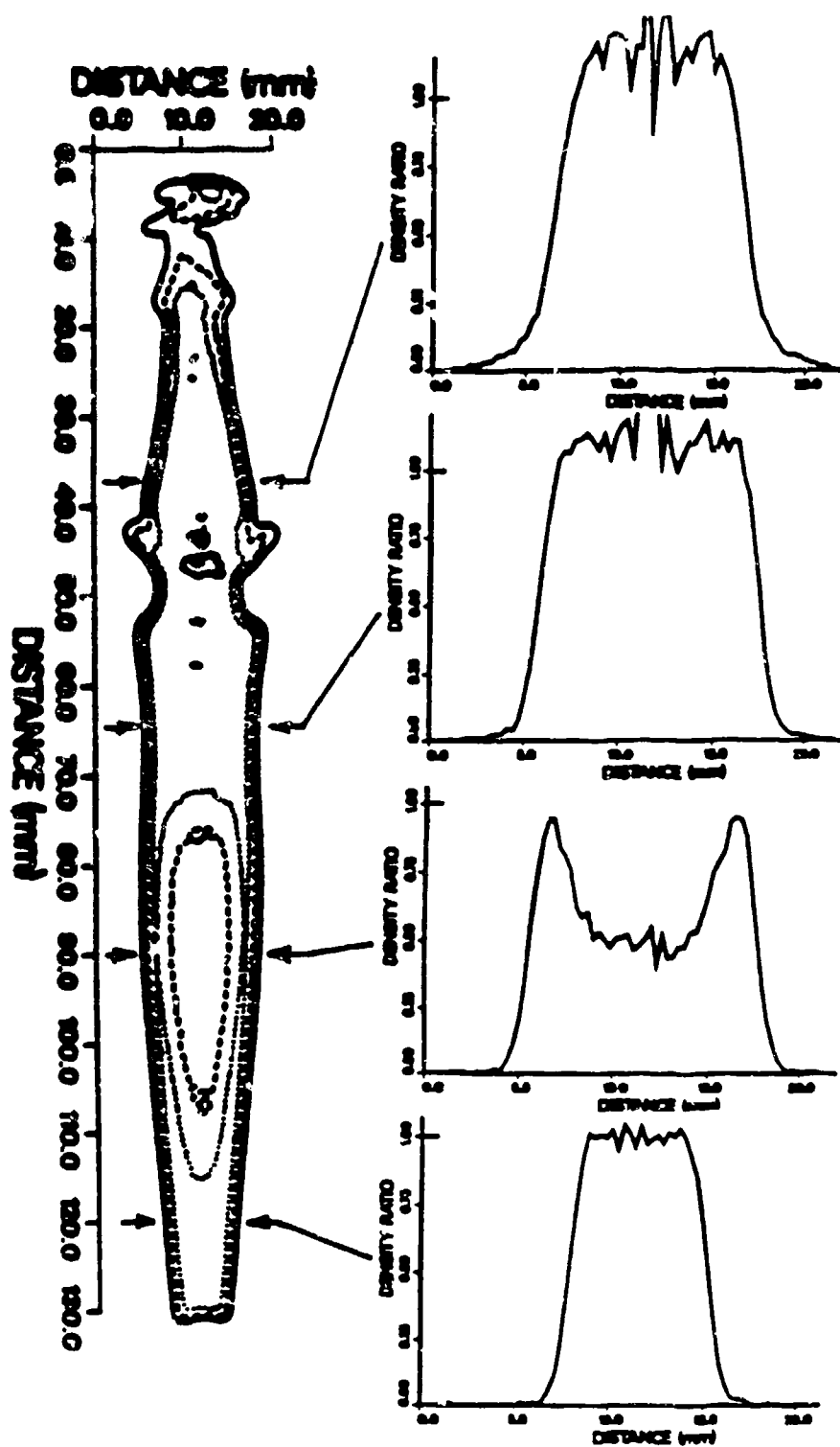


Figure 1. Density profile of a shaped charge in flight several milliseconds after detonation. [Data from Dr. W.J. Carter, Los Alamos.]

dissemination of the results from the Los Alamos work to the DoD community should stimulate many worthwhile investigation.

• Acoustic Microscopy - [Invited Speaker: Prof. B.T. Khuri-Yakub, Stanford]

Acoustic microscopy operates by coupling focused acoustic waves generated by a pulsed transducer operating at frequencies from 1 MHz to 100 GHz through an acoustic lens and a liquid coupling medium (commonly water at frequencies at or below ~2 GHz; liquid helium for frequencies from 10-100 GHz) onto a sample, and imaging acoustic energy at the same frequency reflected and reemitted by the sample. To achieve lateral resolution, the transducer/lens/receiver is scanned across the sample. The interest in acoustic microscopy from the vantage of materials characterization is that it provides, in principal, a method of imaging both internal and surface structures of an object. Moreover, it is a sophisticated extension of ultrasonic part inspection techniques used commonly by certain companies (for example, Aerospatiale) and thus relatively readily acceptable as part of their development and inspection program. Acoustic microscopy is a technique complicated by a number of considerations, and interpretations of the information received by the receiver are not straightforward.

The principal intrinsic tradeoffs in acoustic microscopy are between lateral and depth resolution. High lateral resolution requires a high frequency and short wavelength; high frequency acoustic energy has a shallow penetration depth. The range in lateral resolution extends from 1-2mm at 1MHz to ~0.1 $\mu$ m at GHz (using liquid water as an acoustic coupling fluid) and from ~40nm at 8GHz to ~3nm at 100 GHz (using liquid helium at 0.1°K as acoustic coupler). In appropriate circumstances, the technique has been able to profile steps from 0.5 $\mu$ m to 5nm (with difficulty) and to detect 1 mm test patterns simulating interfacial defects at a depth of 0.25mm below the surface of an otherwise homogeneous material.

The complexity in image analysis stems from the variety of sources of acoustic signals returning from the sample. A pulse of acoustic energy (considered as a wave packet) is generated by the lens, travels through the medium, and strikes the liquid-solid interface separating the coupling fluid from the sample. The energy can be reflected and scattered at these interfaces; it can propagate along the surface as acoustic surface waves and be scattered back into the acoustic coupling fluid and back to the lens by surface features (either morphological, such as steps, or mechanical, such as variations in the acoustic modulus of the sample); it can penetrate the surface and be scattered back to the surface by internal features in the sample. To maximize information from the surface the energy is focused on the surface; to observe the interior of the sample, the energy is focused below the surface. Information can be obtained both from the amplitude and phase of the components of the return signal.

The design of acoustic lenses for particular purposes is an area of active research. A design for topographic profiling, for example, consists of a lens producing a tightly focused spot on the surface, surrounded by a ring that transmits directly to the sample in an annulus around the focal spot without focusing. This outer ring provides a reference signal that is the average over the area of observation; the signal from the focal spot can be deconvoluted from it, and compared with it. For example, as the signal from this type of lens is scanned across a surface having a step, the signal from the reference ring will change slowly and uniformly over the distance corresponding to the diameter of the ring, while the focused spot will change abruptly as it crosses the step. This type of system operates primarily by detecting a phase shift between the reference/ring and observe/focused signal. At 50 MHz, a 24nm step of indium on glass corresponds to a  $7^\circ$  phase shift and is easily detectable; the lateral resolution in this mode is  $\sim 1\text{mm}$ .

Acoustic microscopy can be used to detect and image a number of types of features difficult to detect by other forms of microscopy. Changes in grain orientation of the components of a polycrystalline, polished surface is one example; regions of different residual surface stress in a sample is a second; existence and topography of buried interfaces in a solid is a third. The system would seem attractive for imaging relatively large structure variations ( $>1\text{ mm}$ ) in a number of multilayer or multicomponent systems.

There appear to be opportunities for application of acoustic microscopy. First, it is clear that the technique, in its relatively early stage of development, is capable of providing a variety of types of information about the structures of solids and surfaces, and research acoustic microscopes are now commercially available (although expensive). The technique remains a research technique, however, because signal interpretation is non-routine. The active encouragement of collaborations between potential users of the technique (materials scientists, materials producers) would clearly speed movement of the technique into more widespread use. Second, it seems that there is the opportunity for considerable ingenuity in the design of acoustic lenses for specific purposes --- to generate self-referencing signals, plane waves, pattern-recognizing signals and others. This activity will require sophisticated development of high-frequency acoustic lenses operating at the solid-water interface, and could be highly relevant to a range of Navy concerns. Third, acoustic microscopy seems readily adaptable to the investigation of materials under active stress; its ability to sense anisotropies in acoustic moduli should be particularly useful in this context. It is difficult to predict what information would emerge from this activity, but since failure in many parts probably starts with concentration of stress around surface irregularities, it could be highly useful in detecting critical materials faults before they begin to fail by cracking. Finally, there are clear opportunities to extend the design of microscopes to phase and amplitude sensitive devices in the 1-2 GHz range (the high-frequency end of the water microscope), to (and

perhaps beyond) 100 GHz in the helium microscope, and to automated high speed, low-frequency microscopes for specifically designed materials characterization.

## AGENDA

### NUMERICAL SIMULATION IN MATERIALS PROCESSING

July 20-21, 1987

MRC Organizers: A. G. Evans, A. T. Patera

Monday, July 20      Chairman: A. G. Evans

Opening Remarks, MRC

"Spectral Element Methods for Navier-Stokes" - A. Patera, MRC/MIT

"Finite Element Methods for Processing with Phase Change" - R. Brown, MIT

"Numerical Modelling of Fluid Flow and Heat Transfer in Forming and Welding" -  
R. McLay and G. Carey, Univ. Texas, Austin

Opening Remarks - H. Wisniewski, DARPA

"Fronts Propagating with Curvature-Dependent Speed" - S. Osher, UCLA

"Finite Fourier Transforms That Respect Crystallographic Group Symmetry" -  
L. Auslander, CUNY

"Fractal Modelling of Materials" - M. Bamsley, Georgia Inst. of Tech.

Tuesday, July 21      Chairman: A. Patera

"Constitutive Equations and Computational Procedures for Hot Working of Metals" -  
L. Anand, MIT

"Progress in the Development of HIP Sensors" - H. Wadley, NBS

"Noncanonical Hamiltonian Dynamics of Inviscid Fluids and Nonlinear Stability" -  
H. Abarbanel, UCSD

DARPA's Applied and Computational Mathematics Program - H. Wisniewski, DARPA

Discussion

# ATTENDEES

July 20, 1987

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## INTRODUCTION

The Applied and Computational Mathematics Program is new to the Defense Science Office of DARPA and to the Materials Research Council. This meeting was organized to bring two different cultures together: Applied Mathematicians and Material Scientists interested in the simulation of materials processing.

Actually there were three diverse groups: Material Scientists, Applied Fluid Mechanicians and Applied Mathematicians. Each group had a somewhat different view of what and how the Mathematics Program could be utilized, but it was a very fruitful exchange and plans were made for a two day session in the 1988 Summer Conference to deal with boundary layers, shocks, shear bands and singularities.

The Council would suggest that an Advisory Committee be formed to assist the Program Manager in making the connections between applications and the program elements. They also suggest that the Digital Wind Tunnel program be coordinated with NASA efforts and DARPA's needs and expectations be more carefully defined.

## NUMERICAL SIMULATION IN MATERIALS PROCESSING

A. T. Patera

### SUMMARY

Briefly summarized, the invitees spoke on:

Session 1: (A. Patera) numerical methods for high Rayleigh number unsteady flows, with application to bulk flows in Bridgman and Czochralski systems;

(R. Brown) numerical methods for moving boundary problems, with application to complete (dynamic) Bridgman and Czochralski systems;

(R. McLay) numerical methods for welding and forming, with emphasis on surface tension and deforming domains.

Session 2: (S. Osher) numerical methods for hyperbolic problems involving fronts propagating with curvature-dependent speed, with emphasis on accurate treatment of kinks and recombination;

(L. Auslander) fast Fourier transforms that honor crystallographic group symmetry, with emphasis on algorithm design and implementation;

(M. Barnsley) use of iterated function systems for image compression and representation, with emphasis on algorithms and possible applications.

Session 3: (L. Anand) constitutive equations and computational procedures for hot working of metals, with emphasis on comparison between numerical simulation and experiment;

(H. Wadley) HIP modeling and sensors, with emphasis on interaction/control between computational models and experiment/real-time data acquisition;

(H. Abarbanel) nonlinear stability for Hamiltonian systems with application to inviscid flows.

The discussion period began with an overview of the DARPA ACMP Program by H. Wisniewski, and closed with an interdisciplinary discussion on the numerical solution of singular or singularly perturbed problems (discussed in greater detail below).

## COMMENTS

1. The solution of a large number of materials processing problems requires the development of numerical methods that can treat full time-dependent, three-dimensional, moving boundary fluids problems. These methods are now close at hand, with the potential to predict the performance of both subsystems (e.g. bulk flows) and complete systems (e.g. Czochralski pullers). The methods of choice appear to be finite-element based. High resolution/costly computations will certainly be required for accurate calculations, however advanced, resource-efficient parallel computer architectures should (and are) improving the situation. Graphical representation and physical interpretation of three-dimensional results remains a problem.
2. As numerical methods improve, the limiting factor as regards the validity of numerical predictions will become the lack of understanding of thermophysical properties and interface physics. From discussions at the meeting, it appears that material scientists and fluids modelers are eager to collaborate in relating experiment, physical models, and numerical simulations for certain canonical interface problems (e.g., wetting, meniscus effects), and thus this situation may improve in the near future. Thermophysical properties have only played a secondary role in simulations to date, as zeroth order effects such as numerical resolution have, of necessity, been the first priority.

3. The presentations on metal working indicated that current numerical simulations of plasticity are limited both by incomplete knowledge of the constitutive laws, and the inability of numerical schemes to deal effectively with the "hyperbolic parts" of the domain. In the discussion period this led to active dialogue between fluids, solids, and mathematics researchers as regards the general problem of numerical treatment of singularly perturbed or singular systems; we include a short proposal for a session on this topic at next year's MRC meeting.

4. The ACMP contractors that gave talks presented mathematical and engineering results that had varying degrees of obvious relevance to materials processing (e.g., the Auslander work had obvious immediate application, whereas the Barnsley work did not). It is, of course, possible that in several years all of the abstractions, algorithms and concepts presented will have major impact on materials processing; as the mathematicians realize the potential and range of their ideas, and the materials scientists attempt to view or reformulate their problems in terms of these constructs, significant mutual benefit could result. It should be noted that this last comment is generally true of much mathematical research, and is not restricted to the particular mathematical concepts presented by the ACMP invitees.

## AGENDA

### SYNTHESIS, PROCESSING AND APPLICATIONS OF HIGH $T_c$ SUPERCONDUCTING MATERIALS

July 22, 1987

**Objectives:** This workshop is intended to identify problems in processing and synthesis of high  $T_c$  superconductors, to suggest plausible applications for these materials, to review current theoretical rationalizations of their behavior, and to suggest possibilities of developing new compositions having improved properties.

Chairman: G.M. Whitesides

Introduction - K. Rhyne, DARPA

Synthesis - A. Stacey, Berkeley

Chemistry - E. Wasserman, duPont

Processing - R. Poeppel, Argonne

Theory - H. Ehrenreich, MRC/Harvard

IR Detectors - M. Kinche, Texas Instruments

Mechanical - H. Kolm, Electromagnetic Launch

Signal Processing - R. Withers, Lincoln

Discussion

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July 22, 1987

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Rice, J.	Harvard/MRC	

- EXECUTIVE SUMMARY -  
HIGH  $T_C$  SUPERCONDUCTORS

G. M. Whitesides, M. S. Wrighton, and H. Ehrenreich, Organizers

Objectives of the Workshop

1. To identify specific electrical, magnetic, optical and mechanical components as targets for a research and development program intended to evaluate the strengths and weaknesses of ceramic high  $T_C$  superconductors, to provide the data concerning physical properties required to design devices based on them, and to develop techniques for their production and fabrication.
2. To establish the types of scientific information that will be required as the basis for rapid development of technologies using these materials.
3. To address the issue of whether the current high  $T_C$  superconducting materials ( $YBa_2Cu_3O_{7-\delta}$  and analogous structures) are the proper focus of the DARPA activities, or whether new materials with improved properties have, or will soon, appear.

DoD Relevance

The high  $T_C$  superconductors are a scientific revolution. Will they also form the basis for a technological revolution? Sufficiently little is known about the properties of these materials to be able to predict their ultimate utility. Existing materials may be useful in microelectronics (power distribution lines, low-loss components for high frequency circuits, densely packed Josephson junction arrays), in optics (IR detectors), in magnets (small, efficient motors), and in moving systems (levitators, bearings). Development of fabrication techniques that would maximize the potential of the existing systems might yield new devices such as superconducting thrusters, magnetic quench guns, and small, quiet electromagnetic propulsion systems. The development of new materials with  $T_C > 400^\circ\text{C}$  would almost certainly revolutionize all aspects of the military

and civilian economy, by displacing a wide variety of existing systems for generating, transmitting, and storing and using electrical energy.

### Technical Summary

The one-day workshop covered a number of topics relevant to high  $T_c$  materials: synthesis, processing, theory, IR detection, mechanical and microelectronic applications. These features emerged:

1. YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> is the best presently available material. There are hints of new materials with higher values of  $T_c$ , but none is firm. Theoretical considerations indicate no fundamental limit to  $T_c$ , however, and a material superior to YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> may appear.

2. The processing of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> will be very difficult. Issues include achieving useful long-range lattice order in a very anisotropic material; achieving the proper concentration of lattice oxygen to maximize electrical, materials, and chemical properties; conducting the annealing steps required to fabricate the material under conditions compatible with other components; selecting these components to be unreactive toward the highly reactive ceramic; protecting the material from spontaneous decomposition (if this proves a problem) and reaction with its environment; developing strategies for strengthening and toughening it.

3. Many components of the science base required for rapid development of technologies based on high  $T_c$  materials must be developed. Understanding their thermodynamic and kinetic stability, their crystal growth, their very high ionic mobilities (especially of oxygen), their reactivity toward environmental and systems components, and the relationship of all these factors to  $T_c$  and the critical current are particularly important.

### Suggestions for DARPA Action

1. A number of components represent good targets for prototyping designed to evaluate critical physical, electromagnetic, optical and chemical properties. Data obtained from these components would make possible the realistic evaluation of applications, and guide design and engineering. DARPA should develop these components:

- i) Microelectronic power distribution line, to evaluate the critical current and to test fabrication techniques,
- ii) Strip line, to evaluate high frequency performance (especially loss),
- iii) Magnets, to evaluate the capability of wire-wound, bitter plate and unconventional designs, and to establish achievable magnetic field strength,
- iv) Josephson Junctions, to explore microfabrication technology, and establish packing densities and properties achievable with these materials,
- v) Bearings, to develop technology for fabricating mechanically functional shapes with high tolerance in shape, mechanical properties, and magnetic properties,
- vi) IR Detectors, to evaluate a number of electronic properties, including band gap, carrier concentration, and carrier mobility,
- vii) Ceramic Capacitor, to test the utility of the high  $T_C$  materials as current carriers in non-superconducting mode,

2. DARPA should actively monitor these development programs to identify technical/scientific issues that require solution, and intervene to make certain that development proceeds in parallel on all critical issues. DARPA should take

responsibility for coordinating test protocols so that results obtained in different laboratories can be compared, and generally take an active role in management and coordination to try to minimize duplication of effort.

3. DARPA should support those parts of the science base that are directly relevant to the development of technology: studies of the thermodynamics of the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  system of compounds, of the kinetics of relevant reactions of these compounds, and of oxygen (and other ion) migration in the lattice are particularly important.

4. The most significant applications of superconductivity at 90°K, or of the electromagnetic or optical properties of the  $\text{YBa}_2\text{Cu}_3\text{O}_n$  family of ceramics are probably not now obvious. DARPA should encourage innovation and experimentation, especially at the device level, and not fix so rigidly on objectives specified at this early stage that its contractors miss good but unconventional applications.

## HIGH $T_C$ SUPERCONDUCTORS

H. Ehrenreich, G. M. Whitesides, and M. S. Wrighton

This workshop was focused on the broad problem of processing and fabrication of high  $T_C$  superconducting materials. Its principal concerns were these:

- i) What should be the objectives of a program intended to bring high  $T_C$  materials to the stage of prototype components and/or devices as rapidly as possible?
- ii) What components and devices represent plausible and technologically profitable targets?
- iii) What kinds of scientific and engineering data are needed before it is possible to identify accurately the areas in which the performance of the high  $T_C$  materials will give unique performance to systems?
- iv) Which objectives fit best with specific systems requirements of the DOD? Which are more generically relevant to the manufacturing economy of the U.S.?
- v) Is the current family of ceramic high  $T_C$  materials ( $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ) the best candidate for manufacturing development, or are there (or will there soon be) new materials with better properties (especially higher values of  $T_C$  and critical currents?)

The general consensus of the meeting was that the high  $T_C$  materials represent, without question, a major (possibly even revolutionary) scientific advance. Before their discovery, there were substantial doubts that it would ever be possible to prepare materials showing superconductivity at other than very low temperatures. After their discovery, there is no current theoretical reason to believe that it is impossible to have superconductivity at high temperatures ( $T_C$  @ 400°K?). Further, the discovery of high  $T_C$  superconductivity in a ceramic material, while not entirely unanticipated was certainly astonishing. Thus, the high  $T_C$  ceramic materials represent a paradigm-destroying discovery, and are forcing a rethinking of the entire field of superconductivity.

In practical terms, however, the impact of these materials is less immediately obvious. The technology of superconductivity at 4° K is well established, and has had important influence on magnet design and on specialized magnetic devices (SQUID devices) and forms the basis for promising electronic devices (Josephson junction based systems). The range of application of low-temperature conventional superconductors has, in practice, been relatively modest. The high  $T_c$  devices have the attractive characteristics that they operate at liquid nitrogen temperature rather than at liquid helium temperature, and that they have, in principle, high values of critical field. They also have a number of serious disadvantages relative to conventional superconductors, including low mechanical strength, difficulty in manufacture, high chemical reactivity, unknown thermodynamic stability and operating lifetime, highly anisotropic properties, and generally difficult character in terms of ease of manufacture (even for a ceramic). Thus, while it is clear that a superconductor that would operate at room temperature reliably (that is, one having  $T_c > 400^\circ\text{C}$ ) would have truly revolutionary impact on technology (almost regardless of the difficulty of manufacturing products from it), the technological impact of the current generation of high  $T_c$  materials will depend on detailed comparison of properties and economics with existing systems (both conventional superconductors and normal conductors). As an example of a competitive material, copper shows significantly decreased resistive losses at 77°K relative to room temperature, and is very much easier to manufacture than ceramics. Evaluating the characteristics and properties of the high  $T_c$  materials in sufficient detail that it will be possible to recognize their proper application, developing the technology for their manufacture to the point that realistic economic evaluation of their cost is possible, and evaluating cost/performance ratios for them for comparison with other materials are important objectives of the DARPA program.

The speakers invited to address the workshop covered a range of areas of expertise, from chemical synthesis to optical, mechanical, and electronic applications.

Synthesis [A. Stacy, Department of Chemistry, U. California at Berkeley].

The high  $T_c$  materials are structurally complex layered ceramics with two distinguishing chemical characteristics: important lattice oxygen deficiencies (and high lattice oxygen mobility) and a high concentration of the constituent copper in the form of copper (III). A wide range of synthetic techniques can be applied to the synthesis of these materials: intimate mixing of powders of the component materials followed by heating; precipitation of solids with the correct ratio of Y, Ba, and Cu from solution, followed by heating; sol-gel methods; evaporation and reactive cosputtering; oxidation of alloys, and others. All of these methods work more or less well, and there is, at present, no clearly defined "best" method.

The technologies of synthesis and fabrication are sufficiently advanced that it is possible to identify at least some of the issues that will have to be addressed in synthesizing and using these materials. The most important in the short term is probably the different temperatures required to sinter the materials and to adjust their oxygen content to the value desired for superconductivity. Sintering seems best achieved around 900° K. Below ~750°K it gives unsatisfactory results; above 970°K decomposition of the lattice occurs to new systems that cannot be reconverted to the superconducting state. The problem of identifying the optimal conditions to achieve a highly ordered layer structure has not been solved. The material resulting from this high-temperature sintering is not superconducting.

Following sintering the material must be equilibrated with  $O_2$  at lower temperatures (around 550°C). Again, the processing window is narrow. This equilibration results in uptake of oxygen by the lattice, and conversion of the material to

its superconducting form. It appears that the oxygen composition can range from  $\text{YBa}_2\text{Cu}_3\text{O}_{\sim 6}$  to  $\text{YBa}_2\text{Cu}_3\text{O}_{\sim 7}$  with the  $\text{O}_{\sim 6}$  non-superconducting and the values somewhat below  $\text{O}_{\sim 7}$  being superconducting. Calorimetric techniques (especially temperature programmed desorption) seem to offer excellent methods of following these cycles of oxygen uptake and loss.

Critical, unresolved issues concerning these materials deal with their thermodynamic and kinetic stability over the range of conditions for synthesis, processing and use, the apparent ease with which oxygen can enter and leave the matrix and the necessity for it to do so under current processing protocols, and the narrow temperature window for processing. The questions of whether any of the materials so far prepared represent true thermodynamic minima, or whether they are simply kinetically relatively persistent but unstable structures moving more or less rapidly and irreversible toward non-superconducting phases, both remain unanswered. Answering the array of questions surrounding the issues of stability and kinetics is critical to all efforts to design manufacturing protocols and to predict fields of application.

Among other identified problems in processing the  $\text{YBa}_2\text{Cu}_3\text{O}_x$  materials is the difficulty in avoiding phase separations, especially into low-melting, non-superconducting barium and copper rich phases, the necessity to avoid prolonged contact with  $\text{H}_2\text{O}$  and  $\text{CO}_2$  (the latter can form metal carbonates by reaction with the basic oxides), the general difficulty in working with the deliquescent barium salts, and ambiguities in identifying superconducting phases. In connection with this last subject, the Meissner effect seems to provide a much more reliable test of superconductivity than does four-probe measurements of resistance.

One experiment related to the Meissner effect suggests another problem. A torus of sintered  $\text{YBa}_2\text{Cu}_3\text{O}_{6.8}$  was constructed, placed in a magnetic field, and cooled to 77°K. Magnetic flux lines passing through the torus should be trapped as the material

becomes super-conducting; and, in fact, on removing the external magnetic field, the torus showed a residual magnetic moment. This moment was, however, isotropic, and indicated that persistent current was not flowing coherently around the circumference of the torus, but instead was localized (and apparently randomly oriented) in smaller regions. These experiments should not be taken too seriously at present, but they do indicate potential problems in generating the types of geometrically defined persistent currents that might be used in certain types of energy storage devices.

Examination of the structure of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.8}$  by transmission electron microscopy was very successful in single atom imaging (as might be expected of a structure with strong scatterers such as Y and Ba). The presently available photomicrographs show a number of types of parallel lattice structures, as well as boundary regions of complex structure separating ordered and disordered regions. The quality of these pictures clearly indicates the potential utility of high resolution microscopy in exploring problems in lattice structure.

Experiments involving exchange of  $^{18}\text{O}$  for  $^{16}\text{O}$  in the lattice showed a small isotope effect on  $T_c$ : 75% substitution of  $^{18}\text{O}$  for  $^{16}\text{O}$  decreased  $T_c$  by approximately  $1^\circ\text{K}$ . This result, while small, is probably correct, and indicates at least some contribution to superconductivity from phonon mechanisms.

An interesting and potentially useful and important characteristic of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$  is that the material appears to operate close to a metal-insulator transition. Small differences in composition (and temperature, close to  $T_c$ ) are capable of driving the material into an insulating form. This characteristic obviously poses problems in handling and operating the materials, but may also offer opportunities for new types of devices or applications in which closely proximate regions with matched lattices have very different electrical/magnetic properties, by virtue of oxide content in the lattice or of temperature.

### Chemistry of High $T_c$ Materials from the Prospective of a Large Chemical Company

[E. Wasserman, E.I. duPont de Nemours and Co., Wilmington].

From the vantage of Dr. Wasserman, the primary need with the high  $T_c$  materials was understanding at the level of fundamental science, and he repeatedly emphasized the importance of governmental support in generating the science base needed to exploit the existing high  $T_c$  materials, and to develop new ones. He also underlined the preception that the management of large chemical companies remained skeptical and unconvinced of the economic importance of these materials, and that, given that managerial climate, it was unlikely that industry would make a large investment in the science base for any high  $T_c$ -derived technology, at least until large markets were well-defined.

### Processing of High $T_c$ Superconducting Materials [Roger B. Poeppel, Argonne National Laboratory].

The physical properties of the high  $T_c$  ceramics makes them exceptionally difficult to process, even among ceramics, which are themselves intrinsically difficult to process. The high  $T_c$  materials are brittle; temperatures required for sintering of their powders give little margin before irreversible destruction of the lattice occurs; they are highly anisotropic in both structure and physical properties, and the development of techniques for control of lattice / grain alignment is just beginning (primarily using magnetic alignment techniques); they are reactive toward water and  $CO_2$  in some, incompletely understood, circumstances; at high temperature they are highly corrosive, and dissolve components from many types of containers with unknown consequences for the electrical properties of the resulting materials; their thermodynamic and kinetic stabilities under processing conditions are poorly understood, and it is accordingly difficult to predict the result of particular processing conditions; the requirement for a high-

temperature annealing step poses potentially serious problems of compatibility with many components (metals, silicon, organics) of electronic devices.

These problems notwithstanding, Argonne National Laboratory has embarked on a serious program to develop technology for processing high  $T_c$  precursor powders into representative forms: wire, tape, rods, disks, and others. The starting material for this activity is a precipitated oxide mixture of  $Ba^{+2}$ ,  $Y^{+3}$ , and  $Cu^{+2}$ , obtained by controlled hydrolysis of organic precursors (e.g., citrates). The drying and initial heating of these materials must be carried out carefully, to avoid segregation of the elements into regions of composition quite different from that desired.

Using normal ceramic processing techniques, it is possible to produce an initial sintered powder (presumably a hydrated  $YBa_2Cu_3O_{6-6.5} \cdot n H_2O$ ) as a reasonable homogeneous material. This material is ground to a powder, and can then be mixed with binders and extruded into wire, rod, or similar forms, or processed in other ways (for example slip casting from water). The final step involves firing, first to sinter and permit development of the ceramic layer lattice, and then at lower temperature to allow oxygen to equilibrate with the interior and achieve the superconducting structure.

Probably the most technically demanding of the forms is wire, and although wire (or more properly thin solid rod) has been produced, it has low flexibility and breaks easily. Larger shapes (thick rod, disk) have greater strength. The final objects seem to have 85-95% of their theoretical compact density: The residual porosity may be critical in allowing dioxygen ready access to the interior of the solid during the annealing step in dioxygen. None of the forms produced (with the possible exception of simple shapes such as disks) has properties that would allow their use with special design consideration in mechanically demanding environments.

An important and unsolved problem is that of reactivity toward water. Certain samples of fired material survive prolonged exposure to water without serious loss in

properties; other, superficially indistinguishable samples dissolve rapidly on exposure to water. The difference between the samples is not known.

Water-stable samples have been used, as a powdered dispersion in water, for slip casting, and the resulting slip-cast forms successful fired to sintered objects. This technology is in a very early stage, but the observation that it is possible (even if, apparently, not reproducibly possible) to use  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  in the form of a water-stable suspension indicates that water-based processing of powders should be practical.

Some physical parameters have been measured on materials produced in this program. In particular, braided wire has shown a critical current density of  $600 \text{ A cm}^{-2}$  (but the wire was physically very weak).

Several other points are worth noting from the Argonne experience. Phase transformations occur at several points in the processing, and the consequences of these transitions for the physical properties of the final pieces is not clear. The reactivity at high temperature of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  is such that it will probably require protection (of presently unknown character) if it is to be fired with metals, or even with ceramics such as  $\text{SiC}$ ,  $\text{Al}_2\text{O}_3$ , or  $\text{ZnO}_2$ . Thus, fiber reinforcement as a method of toughening may require choice of oxidation-stable fibers, and the construction of multicomponent structures of all sorts may require multistep assembly procedures to isolate reducing components from the ceramic when it is at high temperature. There are also indications that certain metal ions (e.g.,  $\text{Ag}^+$ ) can diffuse from electrodes into the lattice, and destroy the superconductivity.

#### High $T_c$ Superconductivity: Background, Speculations, and a Model [H. Ehrenreich (Harvard, MRC)]

Ehrenreich reviewed aspects of what is presently known concerning the physics of these new materials and presented an original model, dubbed the "Plane-Chain

Superexchange" (PCS) model, that can account for the high transition temperatures and other properties of the (1-2-3) compounds.

A brief review of the rudiments of BCS theory was followed by a description of the structures of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and  $\text{La}_{2-y}\text{X}_y\text{CuO}_4$  and how these are reflected in the electronic energy levels or band structures. The Fermi level and hence the Cooper pairing involves Cu-O antibonding states determined principally by electrons in the puckered Cu-O planes. These theoretical predictions are substantially confirmed by experiment. In particular, photoemission experiments are in good agreement with the electronic structure. The nature of the attractive mediating interaction was discussed. There are various possibilities: (1) collective excitations such as acoustic plasmons excitons, and other charge density fluctuations; (2) Bipolarons; (3) Spin density fluctuations similar to those occurring in heavy fermion metals; (4) Site specific pairing linked to the crystal structure; (5) Electron-phonon interactions as in the BCS theory.

The presentation stressed the fact that the details of the crystal structure were likely to be crucial in determining the mediating interaction, and that it was possible to all these mechanisms contribute to the stability of the superconducting state to some degree.

The new PCS model that was outlined has features of types (3) and (4) of those enumerated above. It regards  $\text{YBa}_2\text{Cu}_3\text{O}_7$  to be a valence fluctuating compound involving  $\text{Cu}^{+2}$  and  $\text{Cu}^{+3}$ . The chains are predominantly  $\text{Cu}^{+3}\text{O}^{-2}$  which is isoelectronic with  $\text{Ni}^{+2}\text{O}^{-2}$ ; the planes are predominantly  $\text{Cu}^{+2}\text{O}^{-2}$ . At the temperatures of interest, well below the Neel temperature of NiO, the chain undergoes anti-ferromagnetic fluctuations, which induce spatially localized opposite spin pairings in the CuO planes. In k-space these correspond approximately to Cooper pairs. The attractive mediating interaction between the electrons involved in pairing is produced by the presence of the chains and would presumably be absent if the chains were either

disordered or absent, provided that this interaction is indeed dominant. Numerical estimates of the superconducting transition temperatures and the coherence length are in good agreement with experiment.

The following observations are important in assessing and guiding the future development of high temperature superconductors: (1) Both critical temperatures and currents are very sensitive to the structure and stoichiometry of the crystal structure; (2) the structural units or moieties of significance to superconductivity are less than three-dimensional; (In particular, the electrical conductivity is associated primarily with two-dimensional Cu-O planes; superconductivity, at least within the model described above, requires the existence of one dimensional Cu-O chains) ; (3) There are a number of reasonable physical models emphasizing the intercalated structural features at least to some degree, which predict high transition temperatures; (Physical models are important in their ability to suggest new physical structures or chemical compositions.) (4) The stability of the presently known materials represents an open question: water vapor, oxygen stoichiometry, and impurities are known to affect the physical properties significantly. Encapsulation or passivation may be helpful.

Careful investigations of matters relating to structural stability and reversibility as a function of temperature, oxygen diffusion coefficients, chemical substitutes or additions are required for sound progress of this field and for reliable technological assessment. This must replace the present race among scientists to be "first" in discovering or predicting a given phenomenon, often on the basis of insufficient or uncharacteristically sloppy data or calculations. The present inhibition on communication resulting from personal ambition in an otherwise open scientific community is certainly deleterious.

### Tactical and Strategic Infrared Systems [M. Kinch (Texas Instruments)].

Kinch discussed the potential of infrared detector systems involving superconductors. The systems of importance are: (1) Tactical systems, which have large background fluxes in the two spectral windows determined by the earth's atmosphere; these occur in the 3-5  $\mu\text{m}$  and 8-14  $\mu\text{m}$  spectral ranges, have associated fluxes of  $10^{16}/\text{cm}^2\text{-s}$  and  $10^{18}/\text{cm}^2\text{-s}$  respectively, and are superposed on the ambient 300°K blackbody spectrum. (2) Strategic systems, which are characterized by low background flux levels and a variety of wavelengths in the range 2-30  $\mu\text{m}$ .

The detector performance is background limited (BLIP) by the photon noise. Optical contrast is achievable only if the density of photon generated carriers or currents exceeds that of thermally generated carriers. BLIP conditions imply that the IR system noise be smaller than that of the detector. Quantitatively, for a direct gap intrinsic semiconductor like HgCdTe operated as a minority carrier device in a tactical system, flux-produced minority carrier concentration  $p_\phi$  must be greater than that,  $p_{th}$ , which is thermally produced. Here  $p_\phi = \eta\phi\tau_{min}/t$ , where  $\eta$  is the quantum efficiency ( $\sim 0.7$ ),  $\phi$  is the incident background flux,  $\tau_{min} \sim 10^{-6}\text{s}$  is the minority carrier lifetime, and  $t$  is the detector thickness. Typically,  $t \sim \alpha^{-1}$ , where  $\alpha$  is the absorption coefficient ( $\sim 10^3\text{cm}^{-1}$ ). The thermally generated hole concentration in n-type material is given by  $p_{th} = n_i^2/n_o$  where  $n_i$  is the intrinsic electron concentration which obeys the condition  $n_o p_o = n_i^2 \propto T^3 \exp(-E_g/kT)$ . For the devices under consideration  $n_o \sim 10^{15}\text{cm}^{-3}$ . At IR wavelengths 12  $\mu\text{m}$ , the requirement  $p_\phi > p_{th}$  implies that  $\exp(E_g/kT) > 10^{16} T^3 \phi^{-1}$ . Thus according to Kinch, BLIP operation can be achieved at  $T < 90^\circ\text{K}$  for background fluxes  $\phi \sim 5 \times 10^{16}/\text{cm}^2\text{-s}$ .

Extrinsic semiconductors, e.g., Ga doped Si, are advantageous for strategic systems. These are majority carrier devices; holes are thermally generated in Ga doped Si. Intrinsic thermal generation is negligible. The same analysis, based on the

inequality  $p_\phi > p_{th}$  leads to the condition  $\exp(E_g/kT) > 2.5 \times 10^{23} T^{3/2} \phi^{-1}$ . Thus BLIP is achieved at  $T < 30^\circ K$  for a background flux  $\phi \sim 10^{10}/\text{cm}^2\text{-s}$ .

Kinch uses these results as a basis of comparison with the performance of a superconducting IR detector. In this case  $p_{th}$  corresponds to thermally generated quasiparticles (i.e., thermally dissociated Cooper pairs). As in a semiconductor,  $p_{th} \sim e^{-\Delta(T)/kT}$ , where  $\Delta(T)$  is the superconducting gap. A quantitative expression is given by Parker and Williams (Phys. Rev. Lett. 29, 924 (1972), Eq. (5)).  $p_\phi = \eta \phi \tau / t$  as before. However  $\tau$  corresponds to the lifetime against capture into a Cooper pair of an electron injected into a superconductor by the emission of a phonon. This process has been calculated by Rothwarf and Cohen (Phys. Rev. 130, 1401 (1963)). Also,  $t \sim \alpha^{-1} \sim 100\text{-}1000\text{\AA}$ . According to Kinch the BLIP condition  $p_\phi > p_{th}$  leads to the requirement  $\exp(E_g/kT) > 1.5 \times 10^5 N(o) E_g T \phi^{-1}$ , where  $N(o)$  is the single spin density of states at the Fermi level of the normal metal and  $E_g = 2\Delta(T)$ . Kinch assumes that  $N(o)$  can take on values between  $10^{22}/\text{cm}^3\text{-eV}$  and  $10^{19}/\text{cm}^3\text{-eV}$ . With  $E_g = 0.1\text{eV}$ , which is also characteristic of 123 superconductors  $\exp(E_g/kT) > 1.5 \times 10^{26} T \phi^{-1}$  and  $1.5 \times 10^{23} T \phi^{-1}$ , respectively.

He concludes that (1) superconductors will not replace HgCdTe in tactical systems, but that (2) they may replace extrinsic Si or HgCdTe in strategic systems. In view of the fact that the field is quite new and that others at present have more positive viewpoints regarding IR applications of high  $T_c$  superconductors, these statements should be viewed with some caution until they are independently verified.

#### Mechanical Devices [H. Kolm, Electromagnetic Launch, Inc].

The most important areas of application of currently used superconductors ( $\text{Nb}_3\text{Sn}$ ,  $\text{NbTi}$ ) are in magnets. These magnets are used primarily in research and in clinical magnetic resonance imaging devices, but magnets are ubiquitous throughout

both DoD and civilian systems in motors, solenoids, switches, displays, and many other systems. The sophistication and degree of control required to manufacture electronic devices suggests that very substantial development will be required to introduce high  $T_C$  components into widespread electronics use. In principle, the technical requirements for introduction of a new material into magnets, levitators and bearings are less than those for a micro-electronics application, (although economic constraints are more important), and successful production of magnets would provide a first step toward the important area of motors.

The requirements and driving forces for use of high  $T_C$  materials in magnets are worth noting. In general, the intrinsic thermodynamic cost of maintaining a conventional superconducting magnet at 10°K is not large, and does not provide the major driving force for use of high  $T_C$  materials. Much more important are the very low specific heat of materials at this temperature (and thus the difficulty in maintaining them at low temperature in the presence of any heat source, such as a local normal region in the magnet or a heat leak from the struts, leads, and windows of the apparatus). Further, the auxiliary apparatus for a liquid nitrogen system - - cryostats, heat transporters, switching gear - - also represent a substantial problem in technology development and is not dramatically simpler than that for liquid helium. Nonetheless, in circumstances where size, complexity, or critical magnetic field are important, the high  $T_C$  materials may offer real opportunities. The demands on the superconducting material in terms of current density and materials homogeneity are probably significantly less for magnets than for some other applications.

A plausible approach to the design of magnets would involve the use of technology developed by Francis Bitter in the so-called Bitter magnets (now used for very high-field applications, where strength of the magnetic field elements combined with efficient cooling are critical elements). A Bitter magnet is made by stacking helical plates

of the current-carrying material, interleaved with insulators, to provide a structure in which the path followed by the current is a helical strip rather than a wire. Since the development of wires from the ceramic materials with mechanical strength sufficient to form the basis for a magnet coil is clearly difficult, it may well be that the construction of a Bitter system with ceramic helical disks represents a more attractive target structure than a traditional wire or tape-wound solenoid.

Other relatively simple target components that might be fabricated and tested at this stage in the technology of high  $T_C$  materials are magnetic flux concentrators (a torus of the high  $T_C$  material that excludes flux in its superconducting form, and can be used to concentrate magnetic field) and bearings. Other plausible demonstrations would focus on magnetic levitation and/or transportation.

More sophisticated applications for high  $T_C$  materials in defense applications are abundant, but impossible to evaluate until more is known about their electromagnetic and mechanical properties. Projects that represent conceivable long-term applications are magnetic quench guns, thrusters (for launching, for example, torpedos, aircraft, or missiles), electric motors for submarine propulsion based on relatively small superconducting drive units, and related devices.

In one useful aside, Dr. Kolm emphasized his opinion that the most attractive method of cooling high  $T_C$  materials might not be with liquid nitrogen, but rather with cryogenic units based on supercritical helium. Helium has a critical point of 4°K at 2.25 atm. At higher temperatures and pressures, supercritical helium has excellent heat conduction properties, and avoids the problem of vapor lock that can occur in a liquid nitrogen-based system if boiling accidentally occurs in a closed part of the loop. The good heat transfer characteristics of helium are, obviously, purchased at the price of a cryogenic system that must be designed to operate under substantial pressure.

Impact of Thin-Film Superconductors on High Speed and RF Electronics [R. Withers (MIT Lincoln Laboratory)].

Withers discussed the impact of thin-film superconductors on high speed and RF electronics. The topics included high speed digital interconnects, microwave integrated circuits, wideband signal processing, and the development required for a superconductor technology. It is noteworthy that the RF surface resistance is nearly four orders of magnitude lower in the region  $10^{12}$ - $10^{13}$  for  $\text{YBa}_2\text{Cu}_3\text{O}_{6.8}$  at  $50^\circ\text{K}$  than that of Nb at  $4.2^\circ\text{K}$ . In that frequency range the latter is comparable to the surface resistance of Au at  $50^\circ\text{K}$ .

The present limitation in high speed digital interconnects is speed. Superconductive interconnects will be important for  $> 1$  cm. line lengths. For long interconnects, intelligent designs must consider line capacitance, driver size, propagation delay, and device-to-line impedance matching. There appears to be a clear payoff at the interchip and wafer-scale integration levels. However, the question of AC losses at magnetic fields considerably lower than  $H_{C1}$  has not received adequate attention.

The present limitation of microwave integrated circuits is attenuation. The discussion was limited to Nb-based superconducting technology; presumably there would be improvements along the line mentioned above for a technology involving the 123 superconductors. The lower microwave loss associated with the use of thin-film superconductors in microwave integrated circuits permits the transmitter power and the noise figure to be reduced. Further, it allows the fabrication of dense circuits on thin substrates. The lower millimeter-wave losses make planar circuits feasible to frequencies exceeding 100 GHz.

The length of tapped delay lines appears to limit wideband signal processing. Withers discussed superconductive chirp filters, tapped delay lines, and spectrum

analyzers. Analog signal processing requires low RF loss in long delay lines, thin, low-loss dielectrics, dimensional uniformity and integration with other devices. The development of a hybrid superconductivity / semiconductor technology would appear to be of great potential importance. The impact of superconducting thin films on analog signal processing may be considerable. Long, accurate, tapped delay is unattainable at the required frequencies by other technologies. The integration of mixers, comparators, and logic elements is feasible by use of superconducting thin films.

The science base required for the development of a superconductive thin film electronics technology includes (1) understanding the conduction mechanisms in anisotropic oxides; (2) the fabrication of low-RF-loss films; (3) the development of techniques for low temperature deposition of films on dielectrics and semiconductors; (4) knowing how to passivate substrate and films to ensure device stability and longevity; (5) the fabrication of low loss dielectrics; (6) the identification of materials that can be processed and that function compatibly.

In the 3-5 year short term, one may expect low-RF-loss thin films for high speed interconnects, microwave integrated circuits, and analog signal processing devices. Over the longer term there may be payoffs in tunnel junctions and novel 3-terminal devices.

It should be stressed that these assessments are based on experience with low  $T_c$  Nb-based technology. It is not obvious that the prognosis for thin film superconducting devices based on the new materials will carry over as projected. Indeed, there may be pleasant surprises. At present, a great deal depends on whether it will be possible to fabricate thin films having the requisite high crystal quality and stability in a reproducible fashion.

### Other contributions.

A number of problems concerning the high  $T_c$  materials were the subject of active discussion. The three following sections deal with issues of encapsulation, oxygen migration, and non-superconducting applications. The new theoretical model relating high  $T_c$  to the crystal structure discussed in Ehrenreich's presentation will be published at a later time.

### Encapsulating Superconducting Materials [(J. Stille, Colorado State/MRC)].

Current 1,2,3-perovskite superconducting materials are unstable to water and lose oxygen over time. One method of preventing this degradation would be to encapsulate the perovskite with a material that would prevent loss of oxygen and transmission of water. A polymer with low permeability that could be coated from solution could offer adequate protection.

Listed below are data on representative sampling of different polymers. Polymers from halogenated olefin monomers appear to be the best. Saran is soluble in common organic solvents.

<u>Polymer</u>	<u>Permeability</u>	
	<u><math>O_2</math>, <math>P \times 10^{10}</math> (25-30°)<sup>a</sup></u>	<u><math>H_2O</math>, <math>Q</math> (40°C)<sup>b</sup></u>
Poly(trifluorochloroethylene) (Kel F, xst)	0.025	4.8
Nylons	0.038	180
Polyethylene (high density)	0.51	-
(low density)	3.95	17
Polyvinylidene chloride (saran) <sup>c</sup>	0.0053	4.8

- a.  $P$  = permeability, having the dimensions =  $\frac{(\text{amount of permeant})}{(\text{area})(\text{time})(\text{driving force gradient})}$
- b.  $Q$  = transmission rate, having the dimension =  $\frac{(\text{amount of permeant})(\text{film thickness})}{(\text{area})(\text{time})}$
- c. Saran is a random copolymer of 85-90% vinylidene chloride and 10-15% vinylchloride

An Estimate of the Diffusional Stability of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  [(J. Hirth, Ohio State/MRC)].

While direct measurements of the diffusivity of oxygen in the 123 compound have not been performed, kinetic data are available that permit the diffusivity to be estimated. Viegers et al.<sup>(1)</sup> show that for  $\text{Ba}_2\text{YCu}_3\text{O}_7$  with  $6 < x < 6.9$ ,  $x$  can be reversibly changed between 6 and 6.9 by cooling or heating in oxygen or air from 450°C to 900°C at 4°C/min. Gallagher et al.<sup>(2)</sup> show similar data for heating/cooling rates of 1°C/min but find that complete reversibility of  $x$  is not achieved on cooling from 900°C at 100°C/min (1.67°C/s). Over the above range,  $x$  varies linearly with temperature, with  $(\partial c/\partial T) = 1.28 \times 10^{19}$  at/cc/°C. Thus, for the irreversible case, 1.67°C/s, cooling imposes a concentration change with time

$$(\partial c/\partial t)_{\text{imp}} = (\partial T/\partial t)(\partial c/\partial T) = 1.67^\circ\text{C/s} \times 1.28 \times 10^{18} \text{ at/cc/}^\circ\text{C} = 2.14 \times 10^{19} \text{ at/cc/s} \quad (1)$$

The increase of  $x$  corresponds to filling of the Cu-O "chain" in the basal plane of the orthorhombic structure established by neutron<sup>(3)</sup> and x-ray<sup>(2)</sup> diffraction. The structure suggests that oxygen diffuses (intercalates) interstitially down the empty row adjacent to the Cu-O chain and fills the necessary chain sites as it reaches them, see Fig. 1. The diffusion model corresponding to this leaking pipe picture is mathematically analogous to the quasi-steady state oxidation model of Wagner. As cooling imposes an oxygen deficiency  $\delta c$ , it is resupplied by diffusion as in Fig. 2. The diffusion flux over unit

area  $J = D\delta c/x$  produces an average concentration change  $(\partial c/\partial t)_{\text{dif}}$ , related to  $J$  by  $(\partial c/\partial t)_{\text{dif}}/\lambda$  where  $\lambda$  is the half thickness of the slab into which oxygen is diffusing. When  $x = \lambda$  the required increment of concentration  $\delta c$  will have been supplied by diffusion.

Table 1. Diffusivity of oxygen and relaxation time

$T(^{\circ}\text{C})$	$D(\text{cm}^2/\text{s})$	$\tau(\text{s}), \lambda = 1\text{mm}$
500	$3.70 \times 10^{-4}$	14
400	$1.33 \times 10^{-4}$	38
300	$2.99 \times 10^{-5}$	$167 = 2.8\text{m}$
200	$3.83 \times 10^{-6}$	$1.31 \times 10^3 = 2.2\text{m}$
100	$1.62 \times 10^{-7}$	$3.1 \times 10^4 = 8.6\text{h}$
0	$6.85 \times 10^{-10}$	$7.3 \times 10^6 = 85\text{d}$

Table 2. Diffusivity of oxygen and relaxation times

$T(^{\circ}\text{C})$	$D(\text{cm}^2/\text{s})$	$\tau, \lambda = 1\text{mm}$	$\tau, \lambda = 10\mu\text{m}$
500	$1.23 \times 10^{-7}$	10.1h	4.1s
400	$5.59 \times 10^{-9}$	10.3d	1.5m
300	$2.03 \times 10^{-10}$	285d	41m
200	$1.80 \times 10^{-12}$	87.9y	32d
100	$1.30 \times 10^{-15}$	----	12y

Hence the average diffusional supply is

$$1/2(\partial c/\partial t)_{\text{dif}} = D\delta c/\lambda^2 \quad (2)$$

A similar estimate would be obtained with a simple error-function solution instead of the leaky pipe solution.

The condition for reversible change of concentration is  $(\partial c/\partial t)_{\text{dif}} > (\partial c/\partial t)_{\text{imp}}$  and vice-versa for the development of irreversibility. Hence the onset of irreversibility should occur when  $(\partial c/\partial t)_{\text{dif}} = (\partial c/\partial t)_{\text{imp}}$ , or

$$(\partial c/\partial t)(\partial T/\partial t) = 2D \delta c/\lambda^2 \quad (3)$$

Gallagher et al.<sup>(2)</sup> find that a value of  $\delta c = 2.88 \times 10^{20}$  at/cc develops at 500°C. Similar results were found by Blerdell et al.<sup>(4)</sup> on material locally characterized by a density (92-95%) corresponding to a closed pore structure and hence where essentially bulk diffusion over a specimen dimension of  $\lambda \sim 1$  mm is required for oxygen equilibration. With these estimates Eq. (3) gives

$$D \sim 3.7 \times 10^{-4} \text{ cm}^2/\text{s}, 773\text{K}$$

Estimates of this same order have been made by others<sup>(5)</sup>.

With the typical preexponential value of  $D_0 \sim 1 \text{ cm}^2/\text{s}$ , the above value of  $D$  gives an activation energy  $Q = 11,100 \text{ cal/mol} = 0.480 \text{ eV}$ . With this value of  $Q$ ,  $D$  can be estimated at other temperatures as shown in Table 1. Also listed are the relaxation times  $\tau = \lambda^2/2D$  to appreciably change the oxygen concentration by diffusion when a sample is exposed to a non-equilibrium oxygen environment.

One may speculate on the basis for the rapid diffusivity. First, the view in Fig. 1 suggests interstitial-type diffusion, a type for which similar or smaller values for  $Q$  are observed in metal matrix systems such as H-Fe ( $D \sim 10^{-5} \text{cm}^2/\text{s}$  at room temperature), C-Fe, N-Fe and so forth. With a purely ionic radius of 0.132 nm for oxygen, the activated

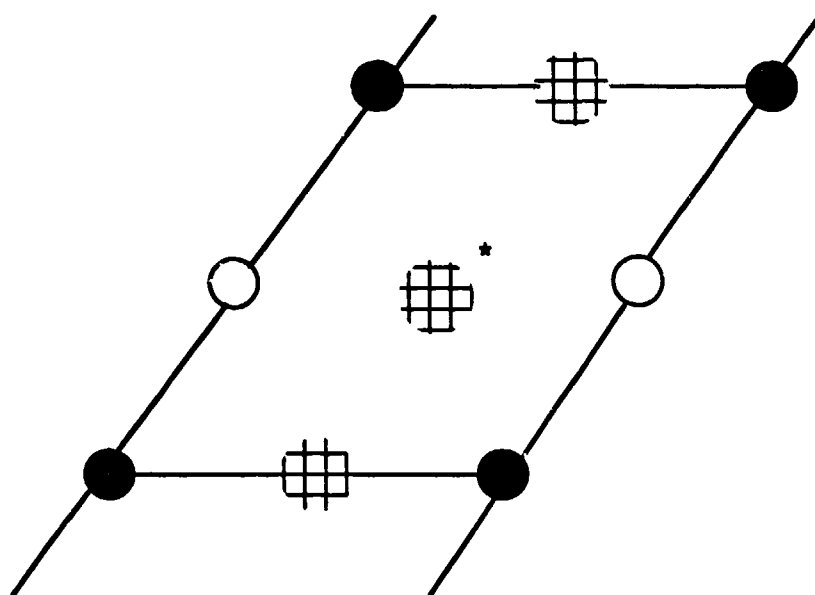


Figure 1. Basal plane of 123 compound with  $\text{Cu}(*) - \text{O}(0)$  chains and the pipe for diffusion of oxygen, with energy minima (#) and the saddle point for a diffusion jump (#\*) both shown.

state in Fig. 1 would suggest a misfit of 19%, suggesting a large strain energy contribution to  $Q$ . However, two qualitative factors would tend to reduce  $Q$ . First, the Cu-O bonding in the chain has a quasi-covalent character which could reduce the effective size of the in-chain oxygen barrier anions. Second, oxygen atoms diffusing into

the empty chain may remain wholly or partly un-ionized, or become neutral as part of the hopping process, until they move into a vacant site in the chain, because they need to acquire electrons by the  $\text{Cu}^{+2}/\text{Cu}^{+3}$  doping reaction.

An alternative is that even at 92-95% density the porosity is partly open, or, equivalently, grain boundary diffusion may provide a rapid diffusion path at 500°C. In such a case the appropriate value for  $\lambda$  would be the grain size, 10  $\mu\text{m}$ , and the factor 1/2 in Eq. (2) would become 1/6 because of three dimensional effects. With these estimates we would have

$$D \sim 1.2 \times 10^{-7} \text{ cm}^2/\text{s}, 773\text{K}$$

and  $Q = 25,400 \text{ cal/mol} = 1.10 \text{ eV}$ . The values of  $D$  for this case are listed in Table 2. Even with this lower value of  $D$ , draining of a surface layer of 1  $\mu\text{m}$  of oxygen would occur in 2 months at 100°C so, particularly for thin film devices, a need for encapsulation is evident. The only ameliorating factor would be an epitaxial film with basal planes parallel to the surface. The model of Fig. 2 implies slower diffusion in the c-axis direction so that such an epitaxial film would leak only laterally.

As a final remark, we note that Viegers et al.<sup>(1)</sup> obtain some indication of rapid ingress and egress of oxygen at 100°C!

### Conclusion

Diffusion of oxygen in the 123 compound appears to be so rapid that encapsulation of the compound by an oxygen/water barrier would be required to prevent potential change of composition and degradation of the compound in superconducting applications.

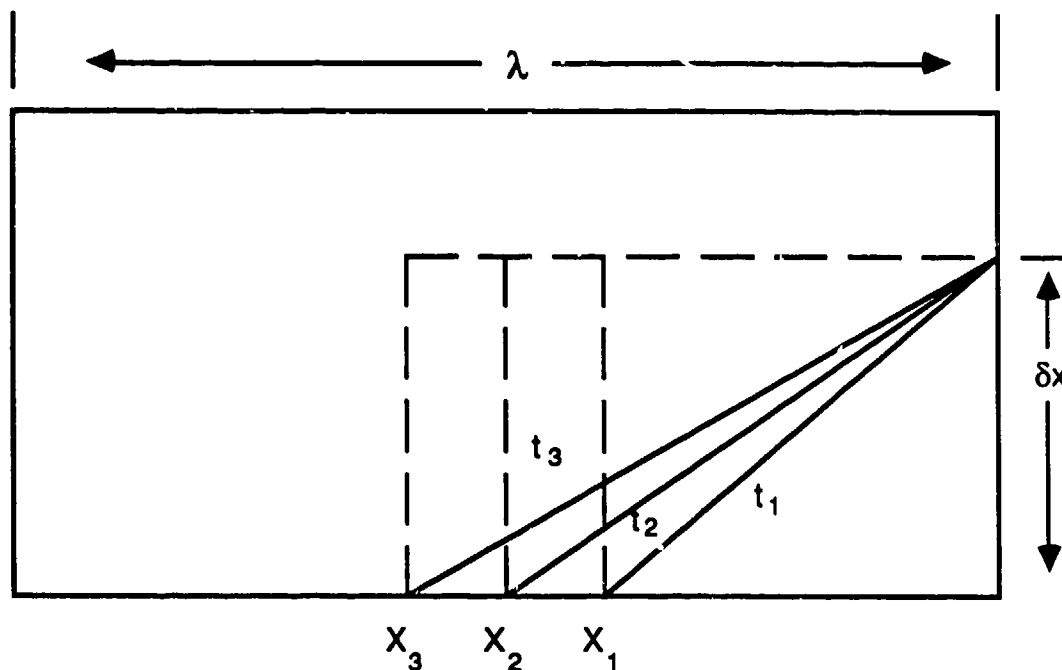


Figure 2. Diffusion profiles in the pipe — and corresponding c-x curves - - - at various times.

#### References

1. M. P. A. Viegars, D. M. de Leeuw, C. A. H. A. Mutsaers, H. C. A. Smorrenburg, J. H. T. Hengst, J. W. C. de Vries and P. C. Zalm, Philips Research Laboratory.
2. P. K. Gallagher, H. M. O'Bryan, S. A. Sunshine and D. W. Murphy, Materials Research Bulletin, July 1987.
3. F. Beech, S. Miraglia, A. Santoro and R. S. Roth, National Bureau of Standards.
4. J. E. Blendell, C. K. Chiang, D. C. Cranmer, S. W. Freiman, E. R. Fuller, E. D. Krasicka, W. L. Johnson, H. M. Ledbetter, L. H. Bennett, L. J. Swartzendruber, R. L. Myklebust, D. S. Bright and D. E. Newbury, National Bureau of Standards.
5. M. F. Yan, AT&T Bell Laboratories.

## Non-Superconducting Uses of $\text{YBa}_2\text{Cu}_3\text{O}_7$ [(L. Eric Cross, Penn State/MRC)].

### General Comments

A very wide range of conventional ceramic preparative techniques have been successfully applied to the production of the  $\text{RBa}_2\text{Cu}_3\text{O}_7$  superconductors, mixed oxide powder methods, chemical coprecipitation using nitrates, oxalates, citrates, sol-gel method etc. The phenomenon appears remarkably forgiving to a wide range of substitutes upon the rare earth, barium and oxygen sites less so to substituents on the copper site. X-ray analysis which appears to be widely used to characterize the structure is very insensitive to small second phase inclusions and one doubts whether many of the samples prepared are in fact phase pure or chemically pure. Ideas as to the thermodynamic stability of the 123 compound under different ambients appear 'hazy' at best. The ceramics discussed were all of very low density (less than 85% theoretical) and would have continuously connected pore structures, permitting rapid 'equilibration' under different oxygen pressures.

The 90-100°K transition to a superconducting state appears to be well defined and reproducible between many different groups. There are many evidences of unusual behavior above 100°K but no completely clear unequivocal verification at time stable superconductivity.

### Possible applications of the oxide superconductor at temperatures above $T_c$ .

The  $\text{RBa}_2\text{Cu}_3\text{O}_7$  compositions may be of significant importance as new electrode materials for special electronic applications. One example may be drawn from the Multilayer Ceramic Capacitor industry (MLCs). In current MLCs the dielectric of choice is most often a high permittivity ferroelectric oxide material which must be processed under strongly oxidizing conditions. For MLC applications, economy demands that the conductive electrodes be co-processed with the oxide ceramic, but the need to fire under oxidizing conditions then limits the choice of conductors to platinum or

silver: palladium alloys. These electrode metals often represent more than 75% of the cost of the MLC.

It is possible to modify the dielectric formulation by strong acceptor doping to permit the use of nickel electrodes, but the dopant leads to reliability and degradation problems so that such units represent less than 2% of the current market. In all MLCs, incompatibility in thermal/mechanical characteristic between electrode metal and ceramic leads to significant problems of delamination in the bonded dielectric sheets and all commercial composites are to some extent delaminated.

Processing conditions for many of the dielectric ceramics are compatible with those for the 123 superconductor oxides and one may suggest that for suitable low firing compositions the metallic oxide in its non superconducting state could form an interesting substitute for the noble metals and permit the fabrication of an all ceramic MLC.

Problems being addressed include:

- (1) The formulation of suitable screen printable inks using 123 powders.
- (2) Control of interfacial reactions between the superconductors and the dielectric.
- (3) Development of suitable termination techniques for electrode pickup.
- (4) Life testing for reliability and resistance to degradation.
- (5) Environmental stability of the encapsulated electrode.
- (6) Analysis of the economics of the ceramic electrode.

Later developments could include:

- (1) Development of insulating grain coatings to make barrier layers capacitors from the 123 material.
- (2) Design of new dielectric ceramics for 77°K operation to permit use with the superconducting electrode for possible energy storage.

(3) Use for guarded power plane structure in high density IC packaging.

### Conclusions

Conclusions from this workshop are that  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  and its structural analogs represent a new class of compounds with many remarkable features, most obviously superconductivity at  $>77^\circ\text{K}$ . They are an obvious and important target for active development both of science and technology. These materials have been known for less than a year. It would be unreasonable to expect that their areas of applications would be obvious, or that the problems were only one of applications. If the only applications to the high  $T_c$  materials is to displace  $\text{Nb}_3\text{Sn}$  and  $\text{NbTi}$  from those applications in which the ability to operate at higher temperatures outweighs the difficulty in fabrication, their impact will be small. The sense of the workshop was, however, that the properties of these materials are so interesting that they will generate new applications. Moreover, the prospect can no longer be discounted that materials superconductive at temperatures well above room temperature will be prepared. These materials would truly revolutionize technology, almost regardless of the difficulty in fabricating them. A major effort in superconductivity is justified, if for no reason other than to be prepared in the event materials with  $T_c$  above room temperature are discovered.

## AGENDA

### MRC/DARPA WORKSHOP ON NONLINEAR OPTICAL MATERIALS

July 23-24, 1987

#### Thursday, July 23

Opening Comments - A. Yariv, MRC/Cal Tech

DARPA's Involvement in Nonlinear Optics - J. Neff, DARPA

NSF and Nonlinear Optics - K. Gustafson, NSF

Nonlinear Organic Polymers - J. Meredith, E. I. DuPont

Nonlinear Optical Effects in Polymeric Films - P. Prasad, SUNY-Buffalo

Nonlinear Optical Organic Materials for Device Applications - J. Stamatoff, Celanese

Experiments and Devices with Nonlinear Optical Materials - R. Lytell, Lockheed Palo Alto Res. Labs.

Thin Film Nonlinear Phenomena and Devices - G. Stegeman, U. Arizona Opt. Sci. Ctr.

Basic Material Considerations for Nonlinear Optical Applications - A. Glass, ATT Bell Labs.

#### Friday, July 24

Optimization of Oxide Photorefractive Materials - M. Klein, Hughes Res. Labs.

GaAs Etalons and Waveguides. Bulk vs. Multi-Quantum Wells - H. Gibbs, U. Arizona Opt. Sci. Ctr.

Image Processing and Dynamic Compensation Using Four Wave Mixing - A. Yariv MRC/Cal Tech.

Summary and Discussion

# ATTENDEES

July 23, 1987

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## NONLINEAR OPTICAL MATERIALS

J. Neff and A. Yariv

The purpose of the meeting was to assess the state of the art of nonlinear optical materials vis a vis, DARPA's aims and plans and to help evaluate future actions and directions. There is a large effort in this field within the chemical industry and DARPA has been supplying continuing support to it.

John Neff of DARPA opened the meeting with a description of DARPA's main objectives. These are:

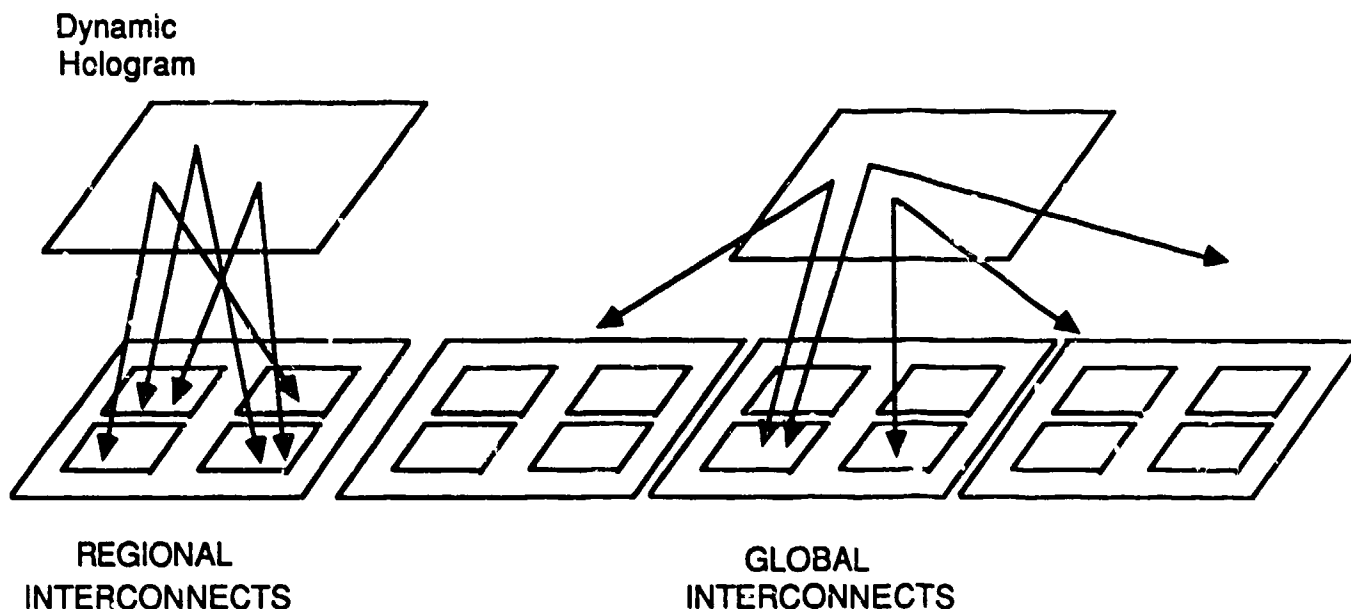
1. Optical Computer reconfigurable interconnects (see Fig. 1)
2. Optical computing
3. Sensor (and eye) protection

J. Meredith of du Pont and J. Stamatoff of Celanese Corporation described the research in their respective corporations on NLO materials. The main effort is to identify molecules with a large  $\beta$  coefficient for applications such as second harmonic generation and electrooptic modulation.  $\beta$  relates the dipole moment of a molecule to the square of the electric field

$$\mu = \mu_0 + \alpha E + \beta E^2 + \gamma E^3 + \dots$$

The prerequisite for a nonvanishing  $\beta$  is that the molecule be asymmetric. Strong correlation has been found between the length of the molecule and  $\beta$  as shown in Table 1. The requisite potential well asymmetry was obtained by attaching a donor complex on one side, usually  $\text{NH}_2$  or  $\text{N}(\text{CH}_3)_2$ , and an acceptor,  $\text{NO}_2$ , on the other.

## RECONFIGURABLE OPTICAL INTERCONNECTS



### HIERARCHY

FIXED OPTICAL INTERCONNECTS:  
(NEAREST NEIGHBOR CONNECTIVITY)

SMOOTHING, MOTION DETECTION,  
EDGE-DETECTION

REGIONAL INTERCONNECTS:

FEATURE EXTRACTION, PERCEPTUAL  
GROUPING, SEGMENTATION

GLOBAL INTERCONNECTS:

OPTICAL FLOW, CONTEXT  
DETERMINATION, MULTI-SENSOR FUSION

Figure 1. Dynamic hologram using a NLO material is used to interconnect and dynamically reconfigure the communication between computer chips.

# Molecular Structural Control of $\beta$

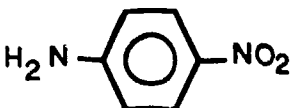
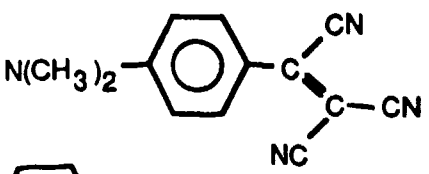
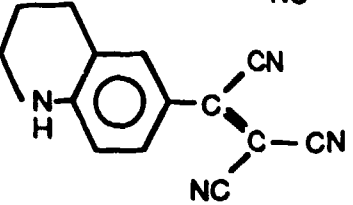
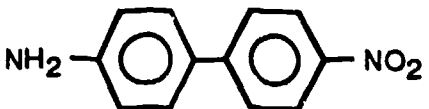
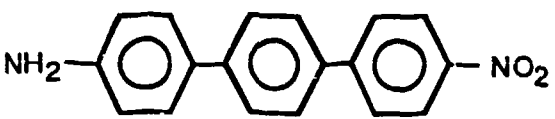
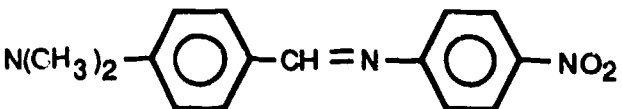
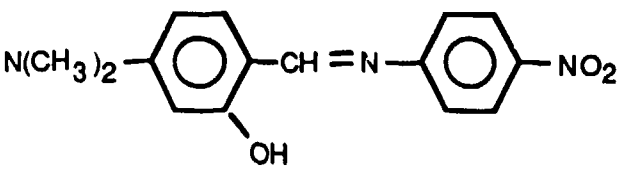
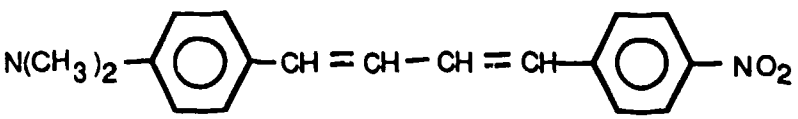
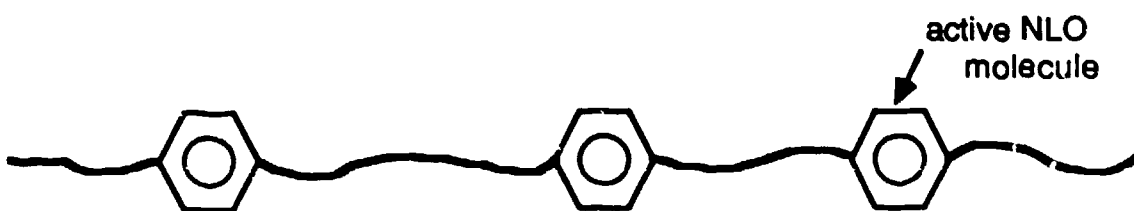
Structure	$\beta$ at 1.9 $\mu\text{m}$ ( $\times 10^{-30}$ esu)	Comment
	5.7	Standard
	21.4	Group
	41.3	Group
	20.1	Length
	50.7	Length
	23.4	Planarity
	61.6	Planarity
	111.2	All

Table 1. The second order molecular polarizability in a number of organic molecules.

The second step in synthesizing a NLO organic material is to embed the NLO molecules in a host matrix and maintain their relative alignment so that the resultant dipole of many molecules does not average out to zero. This has been done using a variety of schemes one of which is illustrated in Fig. 2.

### Incorporation of Active Moieties Into Polymers

- Dissolve the active species in the polymer - guest/host
- Combine the active species into the backbone of the polymer - main chain



- Combine the active species into a side chain of the polymer

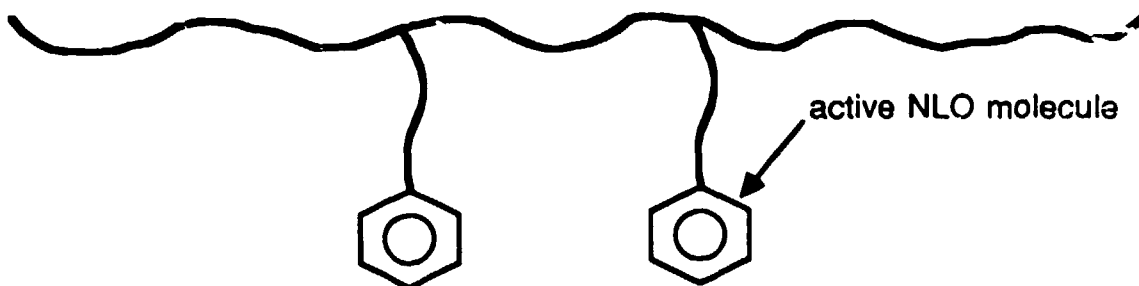


Figure 2. Nonlinear Molecule incorporated into the main chain or side chains of polymers. (Courtesy of J. Stamatoff, Celanese Corporation).

One of the highlights of the meeting was the description, in confidence to the DARPA staff only, of a polymeric organic NLO material with characteristics close or better than those of  $\text{LiNbO}_3$ , which is the best inorganic crystal and thus the benchmark material.

Table 2 summarizes some of the properties of this material which we will call "X".

TABLE 2.

STATUS

- Spin coatable  $\chi^{(2)}$  polymers have been developed
  - suitable for waveguides
  - $\chi^{(2)} > \text{LiNbO}_3$
- Waveguide modulator developed
  - $V_{\pi} \cong 4\text{V}$
  - expect  $V_{\pi} = 1\text{V}$  near term
- Measurements suggest that

$$r = \frac{2\chi^{(2)}}{n^2\epsilon}$$

Table 3 shows the basic parameters and the electrooptic (EO) figure of merit  $n_o^6 r^2 / \epsilon$  of some EO materials. In this table  $r$  is the EO coefficient and the index change caused by an applied electric field  $E$  is


$$\Delta n_o = 1/2 n_o^3 r E$$

while the switching energy per bit is proportional to

$$E_n / \text{bit} \propto \left( \frac{n_o^6 r^2}{\epsilon} \right)^{-1}$$

where  $n_o$  is the index and  $\epsilon$  is the "low" frequency dielectric constant. The column  $E_n / \text{bit}$  gives the approximate switching energy using some basic optimized geometry.

Table 3. NLO coefficients and figures of merit for some common materials.

MATERIAL	$n_o^3 r$ $P_m / V$	$n_o^6 r^2 / \epsilon$ $(E_n / \text{bit})^{-1}$ or $(\frac{P_{\text{mod}}}{\Delta v})^{-1}$	$E_n / \text{bit}$ $j$	$\epsilon / \epsilon_o$
GaAs	43	$1.5 \times 10^{-11}$	$3.3 \times 10^{-11}$	12
LiNbO <sup>3</sup>	320	$2.4 \times 10^{-10}$	$5.2 \times 10^{-11}$	43
BaTiO <sup>3</sup>	$-10^4$	$3.3 \times 10^{-9}$	$4 \times 10^{-12}$	$3 \times 10^3$
 "X"		$\sim 3 \times 10^{-10}$	?	

R. Lytel of Lockheed Laboratories, Palo-Alto, California, reported on a waveguide interferometric modulator with respectable characteristics which had been fabricated on Celanese polymeric material. This is one of the very first real attempts to use organic NLO material in a device configuration. He is also addressing the very important issue of making optical waveguides using polymeric materials. The ability to fabricate waveguides is a prerequisite to any practical applications of these organic NLO materials.

The meeting dealt also with the third order NLO materials, the so called  $\chi^{(3)}$  materials which take advantage of the nonlinear induced polarization

$$P_{NL} = \chi^{(3)} E^3$$

Talks by P. Prasad of SUNY, J. Stamatoff of Celanese and J. Meredith of du Pont all indicated that organic  $\chi^{(3)}$  materials are still in their infancy. There is no reliable theory to predict the appropriate molecular third order hyperpolarizability  $\gamma$  which is related to  $\chi^{(3)}$  by  $\chi^{(3)} = N\langle\gamma\rangle$  and no appropriate modeling. The parameter  $\gamma$  is related to the quartic term  $c$  in

$$V(x) = 1/2 Kx^2 + bx^3 + cx^4$$

of the electron potential function  $V(x)$ . It would follow that long  $\pi$  configured organic molecules with "flat bottomed"  $V(x)$  should display large  $\gamma$ . The chemists are aware of the basic physics but are just now beginning to systematically address it. At present the best  $\chi^{(3)}$  materials are photorefractive inorganic crystals such as  $\text{BaTiO}_3$ , SBN, BSO and GaAs. The ferroelectric crystals SBN and  $\text{BaTiO}_3$  are especially useful because their electrooptic coefficients, which mediate the photorefractive effect, are very large (See Table 4). These materials are used in most of the phase conjugate optics and the image

processing applications. Their main drawback is their long response time. It is found to follow

$$\tau \sim (1/I_0)$$

where  $\tau$  is in second and  $I_0$  the average background optical.

Table 4. Some photorefractive materials.

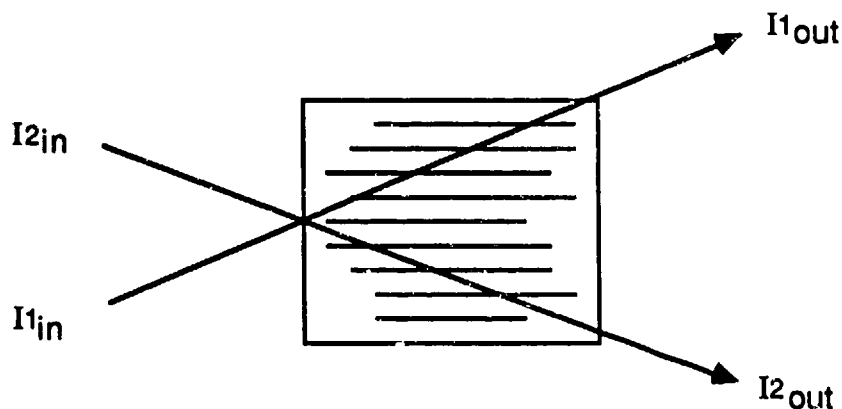
### PHOTOREFRACTIVE MATERIALS

PARAMETER	UNITS	BaTiO <sub>3</sub>	BSO	GaAs
Wavelength Range	$\mu\text{m}$	0.4-1.1	0.45-0.65	1.0-1.5
Dielectric Constant $\epsilon$		3700 ( $\epsilon_{11}$ ) 135 ( $\epsilon_{33}$ )	56	13
EO Coefficient $r_{ij}$	$\text{pm/V}$	1640 ( $r_{42}$ )	4 ( $r_{41}$ )	1.4 ( $r_{41}$ )
$n_0^3 r$	$\text{pm/V}$	~104	~40	~60
No. of Empty Traps $N_E$	$\text{cm}^{-3}$	$2.9 \times 10^{16}$	$10^{-16}$	$10^{15}$
Recombination Time $\tau_R$	s	$10^{-8}$	$10^{-6}$	$3 \times 10^{-8}$
Mobility $\mu$	$\text{cm}^2/\text{V-s}$	$10^{-2}$	$10^{-1}$	6000 = 0.6 MKS)
Photoconductivity $\mu\tau_R$	$\text{cm}^2/\text{V}$	$10^{-10}$	$10^{-7}$	$1.8 \times 10^{-4}$
$\Gamma = \frac{2\pi}{\lambda} n_0^3 r I_m E_{sc} (m-1)$ $\lambda = 1 \mu\text{m} \quad E_{sc} = 10^5 \text{V/m}$	$\text{m}^{-1}$	$2\pi \times 10^3$	25	38

M. Klein of Hughes indicated in his talk that theoretically  $\tau$  should be 2 to 3 orders of magnitude smaller than presently measured values.

A. Yariv in his talk described how the photorefractive effect is used in two-beam coupling experiments to transfer energy from one optical beam to another, see Fig. 3, and how this effect can be used in phase conjugation, image processing and in the construction of optical limiters. The performance of such a limiter is illustrated in Fig. 4. Up to 99% of the energy of an input beam is deflected into the "fanning" direction.

#### TWO-BEAM COUPLING BY PHOTOREFRACTIVE EFFECT



$$I_{1\text{out}} = I_{1\text{in}} e^{\Gamma\lambda}$$

$$\Gamma = \frac{2\pi}{\lambda} n_0^3 r E_{\text{sc}} \approx 60 \text{ cm}^{-1} \text{ in SBN, BaTiO}_3$$

Figure 3. Two-beam coupling in photorefractive crystals.

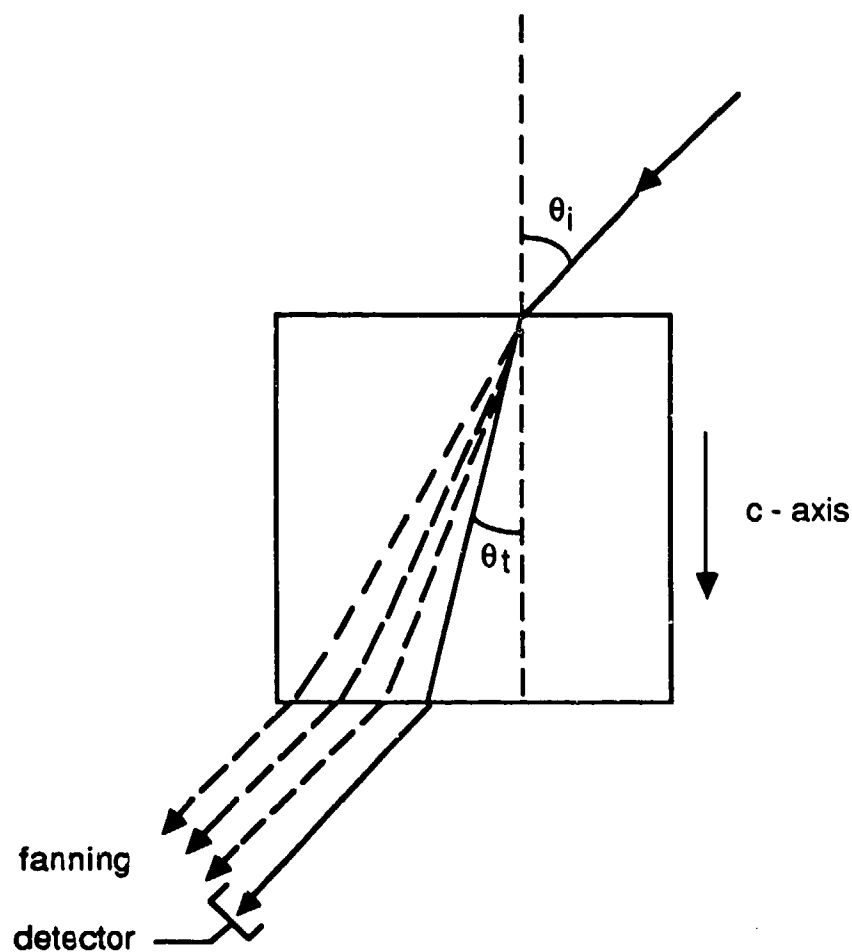


Figure 4a. Fanning limiter crystal showing direction of c axis (defined here as pointing towards the electrode which had been positive when the crystal was poled) and the internal and external angles of incidence. M. C. Cronin Golomb, and A. Yariv, J. Appl. Phys. 57(11), 1 June 1985.

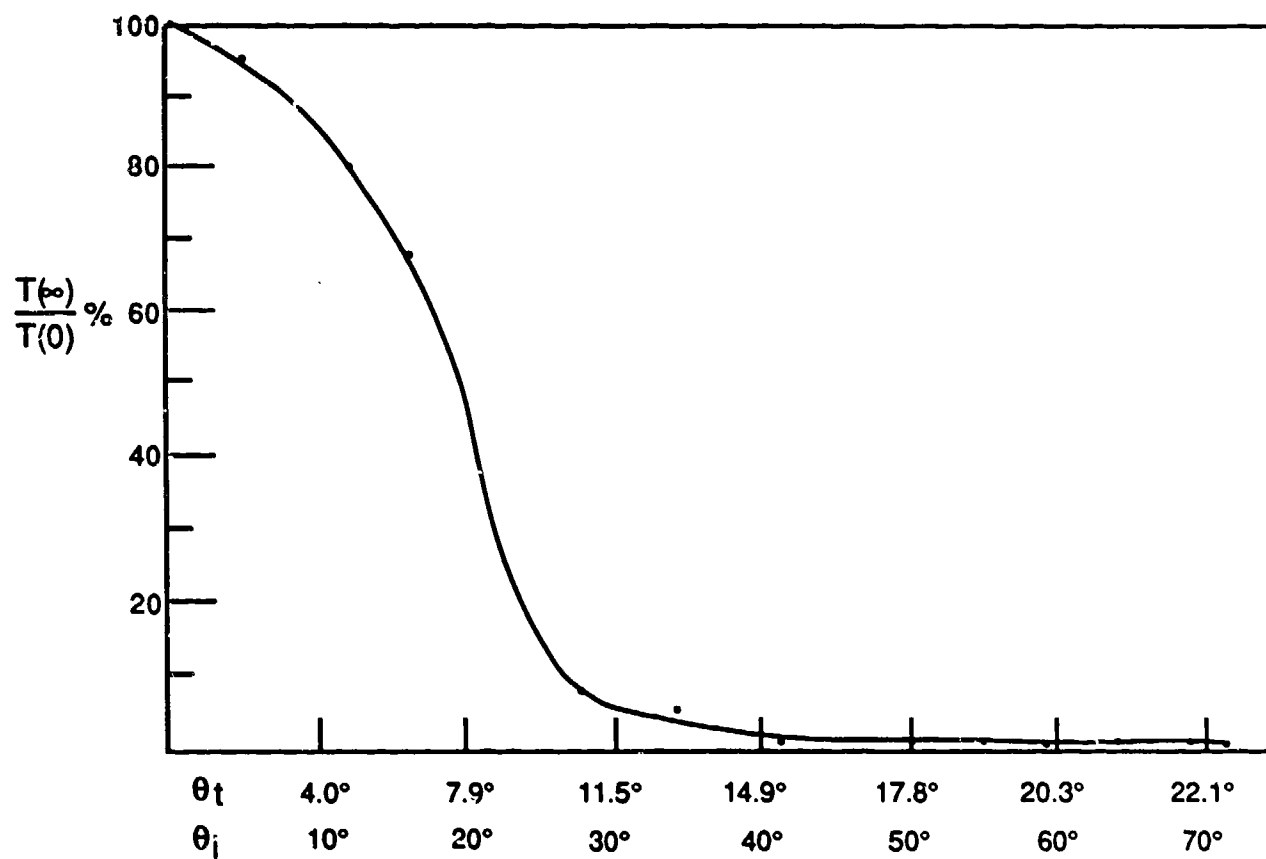


Figure 4b. Transmittance as a function of crystal orientation.

## CONCLUSIONS AND RECOMMENDATIONS

1. Real progress has been achieved in fabricating organic  $X^{(2)}$  materials - there is still a large potential in further improvements in  $X^{(2)}$  to be realized from better orientation and poling of the active molecules in the polymer. At present orientation is only ~1%, an improvement of an order of magnitude or more is theoretically possible. The effort is substantial and well supported by the chemical industry.
2. There is need for a larger level of involvement of the device physicists in working with the new  $X^{(2)}$  materials in fabricating devices. The resulting information should prove invaluable to the material people. We are aware of only one such effort at this time, Celanese-Lockheed.
3. The organic  $X^{(3)}$  materials are at their infancy. They are not getting the same level of attention by the chemical companies as the  $X^{(2)}$  materials possibly because of reduced commercial expectations. The potential is very large and a strong effort both in theory and in synthesis and characterization is needed. P. Prasad in SUNY is one of the few active researchers active in this field, more are needed.
4. The photorefractive crystals offer the best hope at this time for  $X^{(3)}$  applications such as computer interconnects, holographic storage, phase conjugation, image processing and optical limiters for sensor protection. Although, in the case of the ferroelectrics, they are endowed with large effective  $X^{(3)}$  which is sufficient for most applications. They are too slow with response times of

$$\tau(\text{seconds}) \sim \frac{1}{I_0 (\text{watts/cm}^2)}$$

It is not understood at the present time why  $\tau$  is as long as it is and a major effort to try to understand the associated physics and to shorten it could have a large payoff.

## SUGGESTED NEW DARPA PROGRAMS

At the MRC-DARPA presentations held on July 7, Dr. Reynolds outlined the programs currently active in the Defense Science Office. He pointed out that some of these will be maturing and be transferred to other DoD funding agencies or were being picked up and supported by Industry. He asked the Materials Research Council to consider some new areas of research that could be initiated by the DSO.

Four of these were discussed by MRC members and these preliminary programs are introduced in the following papers.

In addition to these there was discussion on where the GaAs program would go now that the current programs are being funded by SDIO. A meeting will be scheduled in Washington in the fall of 1987 to look at the possibilities for actually funding a GaAs based computer system.

DARPA has been funding segments of technology for an Optical Computer System. A Washington meeting will also be scheduled to look at the future of such a computer system.

## COMPUTER SIMULATIONS, VISUALIZATIONS AND MATERIALS PROCESSING

T. C. McGill, D. K. Ferry and A. Patera

Rapid developments are occurring in computers and graphics processors connected to high-performance central processors by very high bandwidth ( $>100$  MBytes/sec) channels. Computers with performance approximating a Cray XMP are becoming available at prices that are greater than an order of magnitude less than those found previously. The cost per megaflop (MFLOP) average performance has roughly been 100K\$ and now is becoming 10K\$/MFLOP. Some of the new systems not only have the performance characteristics described above but also have graphics capabilities approaching the best available in any graphics device that is coupled to a high performance CPU by a high speed data bus.

The arrival of these new systems promises to make it possible to carry out levels of computer simulation, visualization, and materials processing control well beyond anything possible in the past. With roughly an order of magnitude increase in the performance available at the same cost, it becomes possible to carry out realistic computer simulations of a number of processes; use of visualization techniques in the design of processing equipment, devices and materials; and the real-time control of materials processing such as crystal puller, MBE machines, MOCVD reactors to name a few.

The successful completion of this program could result in tremendous improvements in the performance, decreases in the development time, and increases in the ease of manufacture of DOD systems. Since this is largely a US event, the successful application of these technologies could result in substantial increases in the US competitive position.

Hence, we would recommend a highly funded DARPA program aimed at exploiting this very high-leverage, high-payoff area of research and development. Some

of the major points of this program include:

- Placing new high performance computer and graphics facilities in the hands of investigators in these fields rather than computer scientists.
- Developing computer simulations for realistic problems for these new machines (e.g., Czochralski crystal growth, deposition by MOCVD and MBE, etching by reactive ions, beam processing of materials, characterization by SIMS, etc.).
- Developing methods for designing advanced devices and circuits.
- Developing physical models for use in realistic simulations.
- Measuring the appropriate physical, chemical, and materials parameters for these kinds of simulations and real-time process control.

This area offers DARPA a unique opportunity to exploit technology being produced by the strategic computing program and the DSO tech base programs to produce a quantum leap forward in our ability to control and fabricate devices and materials.

## MEETING PROPOSAL FOR 1988 MRC

### II-VI Materials and Devices

**Organizers:** H. Ehrenreich, T. C. McGill, and J. D. Murphy

**Purpose:** To review status and project the prospects of Hg-based materials for IR detector arrays.

#### Topics to be discussed:

1. Materials preparation: discussion of techniques (LPE, MBE, MOCVD, bulk), substrates for films, doping and a categorization of advantages and disadvantages of each.

2. Materials characterization: What kinds of measurements should be made to decide whether or not given materials are suitable for devices? (e.g., minority carrier lifetimes, photo-conductive decay, mobility, surface morphology). If devices are to be fabricated in any kind of quantity, it is not simply adequate to assert that a material is good enough if the device works: yields would be far too low.

3. Materials structures: What are the incentives for bulk vs. superlattices devices? Photoconductive vs. Photodiode devices?

#### 4. Device Questions:

- a) Which device structures and materials are most likely to achieve early success?
- b) What is impeding progress in photodiode based devices?
- c) What are the requirements concerning device fabrication that optimize reproducibility, reliability, and cost?

These questions, for the present, relate only to test structures.

The meeting will emphasize HCT and introduce DMS only to the extent that comparisons can be made. A full-dress discussion of HCT vs. DMS in 1988 is probably premature, although a talk on the subject is desirable.

5. Audience and Speakers

Cognizant industry groups, government agencies and laboratories, universities and MRC. (Possibly one or two from SAT (France), GEC (G.B.)

6. Duration and Numbers

- a) 2 days (1/2 day of which is general discussion)
- b) 7-8 speakers
- c) Attendance not to exceed 25 (including MRC members)

NOTE: Within the allotted time, it will not be possible to discuss all subjects in depth. A prioritized selection needs to be made by the organizers in constructing the actual program. We should know soon at the beginning of 1988 when speakers will be selected.

**Proposal for 2-day session during MRC's 1988 July meeting**

**BOUNDARY LAYERS, SHOCKS, SHEAR BANDS, AND SINGULARITIES**

**MRC Organizers: J. Rice, A. Patera**

A great many problems in continuum mechanics involve equations which are either singular or singularly perturbed. Classical examples of such phenomena are boundary layers in incompressible flow, shocks in compressible flow, shear bands in plastic flow of solids, and cracks in solids. In the latter cases particularly there remain open questions as to how to properly pose problems, and what type of (possibly nonclassical) material constitutive descriptions will be necessary for solutions to exist. Numerical treatment of all of these problems share common foundations and questions: in what (physical or mathematical) norm should the numerical error be small (i.e., is it critical that the structure of the singular region be resolved); if the singular layers are to be resolved, what mesh-adaptive procedures should be used; if the physical phenomena of interest are insensitive to the spatial structure of the singular regions, what numerical methods can be used that avoid unnecessary resolution; can it prove computationally more efficient to soften singularities in order to gain greater regularity, albeit at the expense of regions of rapid variation. By bringing together modelers (including experimentalists) and numerical analysts, many of these issues, often critical to predictive capability, can be addressed.

Note: Boundary layers, shocks, shear bands, and cracks are critical in crystal growth, high speed flows, metal working, and micromechanics of composites, all of which are of current interest to DARPA Materials and DARPA more generally. The speakers would include contractors from the DARPA ACMP.

## OPPORTUNITIES IN ELECTROCHEMICAL SCIENCE AND TECHNOLOGY

G. M. Whitesides, M. S. Wrighton

There now exist several important technological opportunities in the area of electrochemical science and materials science, proof-of-concept laboratory demonstrations of key device concepts, and DoD needs provide DARPA with the basis for a major thrust to develop electrochemical processes and devices. Table 1 lists some of the areas of possible DoD application of the advances made in recent years. In the section below the progress in the chemical and materials science under-lying optimism for development of applications will be reviewed. Some examples of processes and devices regarded as most promising will then be given, along with a description of key concept demonstrations and technical hurdles to development and use.

Several important points regarding background should be made here. First, electrochemical technology is obviously not new and has been used in existing commercial and military applications. For example, electrochemical methods for production of chemicals and metals consumes of the order of 10% of U.S. energy. Table 2 lists some of the existing technology currently available. Second, studies in electrochemistry are intrinsically "device" oriented, every study routinely involves a two or three terminal electrode device. However, what is often lacking in the basic research is the optimization of the performance each electrode in the same medium. Third, studies in electrochemical science are very interdisciplinary. Contributions to progress come from insight concerning molecular synthesis, thermodynamics, mass and charge transport, interface characterization, electrode materials, and heterogeneous kinetics. Fourth, there has been a remarkable revival of interest and progress in electrochemical science, since a cadre of outstanding scientists (from many sub-disciplines) have begun to address challenges in energy conversion and storage, materials processing, and certain

Table 1. Opportunities in Electrochemical Science and Technology

Power Sources

Fuel Cells - ones that use liquid fuels.

Batteries - "integrated" systems infinitely rechargeable.

Capacitors - "super" capacitors, hybrids of existing batteries and capacitors.

Sensors

Microelectrochemical Devices - chemically sensitive analogues of transistors and diodes fabricated as sensor arrays.

Gas Detectors - integrated use of polymeric ion conductors, redox polymers, microfabrication.

Materials Processing

Photoelectrochemical Microfabrication - direct processing of semiconductors using focused laser beams.

Electrochemical Coating - new techniques for coating fibers and powders.

Corrosion Suppression - use new surface modification procedures demonstrated for semiconductor photoelectrodes.

Displays

Electrochromism - make new redox polymers with change in absorptivity of  $10^5 \text{ M}^{-1} \text{ cm}^{-1}$  supercharge in state of charge.

Electrochemiluminescence - exploit understanding of highly favorable, one-electron redox reaction in redox polymers.

kinds of devices based on electrochemistry. Leading workers from the traditional chemistry sub-disciplines of organic, inorganic, and physical chemistry have directed a major fraction of their effort to solving problems in electrochemical science. In summary, the existence of large economic opportunity, the "device" and interdisciplinary orientation of the field, and the intellectual vitality and progress suggest that rapid progress in new and improved electrochemical technologies is possible.

**Table 2.** Some Existing Electrochemical Technologies

**Power Sources**

Lead acid batteries

Nickel/hydrogen batteries

Hydrogen/oxygen fuel cells

**Electrolytic Capacitors**

**Electrochemical Synthesis**

Chlorine

Aluminum

**Sensors and Analytical Chemical Methods**

Medical diagnostics (e.g., glucose and O<sub>2</sub>)

H<sub>2</sub> detectors

Ion selective electrodes

**Electroplating**

# **ELECTROCHEMICAL SCIENCE** **AND TECHNOLOGY**

- **Power Sources**
  - Fuel Cells**
  - Batteries**
  - Capacitors**
- **Sensors**
  - Microelectrochemical Devices**
  - Gas Detectors**
- **Materials Processing**
  - Photoelectrochemical Microfabrication**
  - Coating Technology**
  - Corrosion Suppression**
- **Displays**
  - Electrochromism**
  - Electrochemiluminescence**

## **NEW CHEMICAL AND MATERIALS SCIENCE**

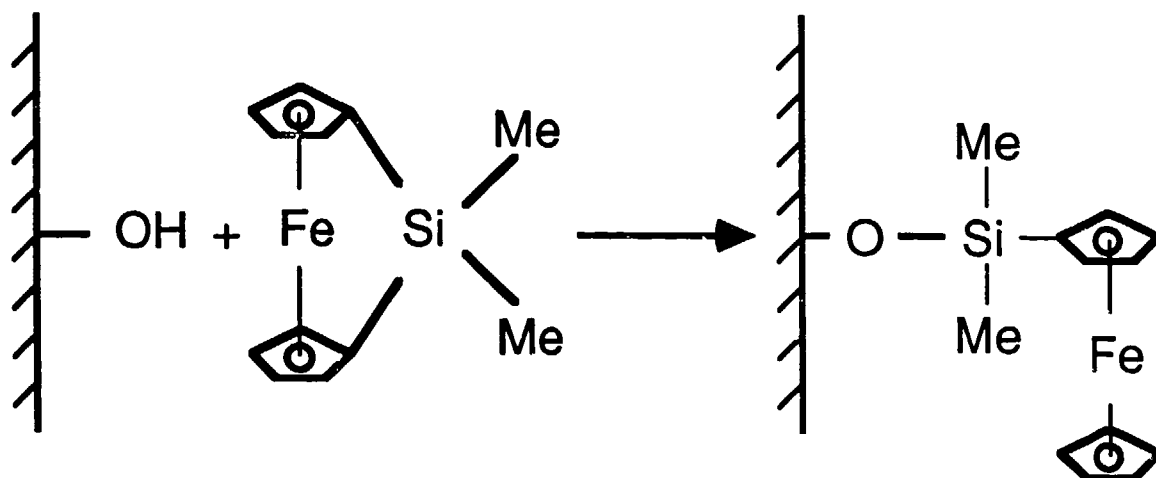
- **Modified Electrodes** - corrosion suppression, electrocatalysis, displays, sensors, energy storage and conversion
- **Polymeric Ionic Conductors** - separators, selective membranes, gas detectors
- **Conducting Polymers** - electrode materials, electrocatalyst supports, microelectrochemical devices, batteries, capacitors, displays
- **Underpotential Deposited Metals** - new materials and properties, contacts, catalysis, sensors

## **NEW CHEMICAL AND MATERIALS SCIENCE**

- **Microelectrodes** - unusual diffusion properties, small RC, sensors, gas phase electrochemistry
- **Heterogeneous Catalysis** - C-H activation, fuel cells, gas detectors
- **Interface Characterization** - XPS, AES, RBS, SIMS, XAFS, SERS, FTIR
- **Microfabrication Science** - surface microstructure, electrode arrays, microelectrochemical devices

## Modified Electrodes

Rational tailoring of surface properties by using chemistry of surface groups.



- Surface chemistry of C, Au, Pt,  $\text{SnO}_2$ , Si becoming developed
- Monolayer and polymer coating techniques now available

## Recent Advances

- Direct "interfacing" of solid electrodes with redox enzymes, implies new synthetic procedures and new sensors
- Modification of microelectrode arrays including via microfabrication techniques, implies microelectrochemical devices, displays, sensors

## Polymeric Ionic Conductors

- Polyethylene oxide/ $M^+X^-$  -  $M^+$  conductor,  $M = Li, Na$
- Polyphosphazenes - Room temperature  $Li^+$  conductors
- Nafion - commercial product,  $Na^+$  conductor
- Polyvinylalcohol/ $H_3PO_4$  - Room temperature  $H^+$  conductor

## Recent Advances

- High room temperature ion diffusion
- Demonstration of "solid state":
  1. Electrochromism
  2. Moisture sensor
  3.  $H_2$  sensor

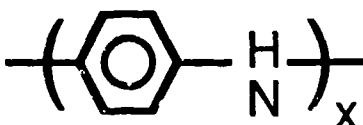
## CONDUCTING POLYMERS

Organic polymers with high electrical conductivity.

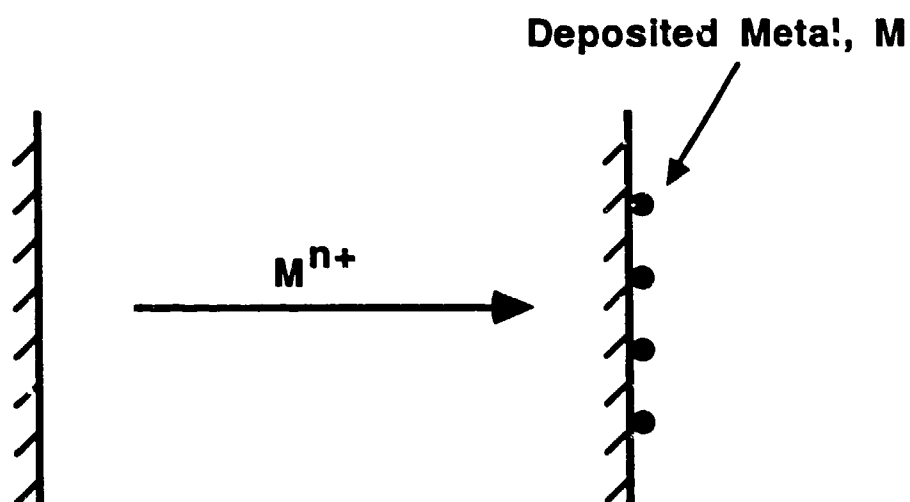
### Recent Advances

- Polyaniline, polyacetylene reported to have conductivity in the range of Cu
- Soluble conducting polymers prepared, implies processing will be possible
- New materials with fixed charges, implies ruggedness
- Demonstration of  $> 10^7$  cycles between "metallic" and insulating state

Polyacetylene - 

Polyaniline - 

## Underpotential Deposited Metals



- Unique structures
- Voltage control, monolayer coverage
- Electrode,  $M^{n+}$  dependent
- UPD metals show unique chemistry

## **HETEROGENEOUS CATALYSIS**

**New understanding of elementary steps in catalysis from studies of solid/gas interfaces.**

- **New understanding can be applied to electrode/electrolyte interfaces**
- **New chemistry of  $\text{>C-H}$  at room temperature suggests major opportunity to develop fuel cell and sensor catalysts**

## **Microelectrodes**

**Dimension of electrode sufficiently small that planar (semi) infinite diffusion does not apply, disks or lines having a small dimension,  $\sim 10\text{ }\mu\text{m}$  or less.**

- **Small double layer capacitance, implies fast response**
- **Small absolute currents allow electrochemistry in "resistive" media:**
  - 1. Gases**
  - 2. Low temperature (77K!)**
  - 3. Alkanes**

## MICROFABRICATION SCIENCE

Preparation of micro- and nanostructures on surfaces via techniques common in integrated circuit manufacturing.



- Microelectrode arrays as "substrates" for further modification
- Controlled "microplumbing", fluidics

## INTERFACE CHARACTERIZATION

### TECHNIQUES USED

XPS, AES, RBS,

SIMS, Microscopy,

XAFS, SERS, FTIR

EPR, XAFS, electrochemistry

ellipsometry, contact angle

### INFORMATION

Structure, composition

morphology, kinetics,

durability, coverage

dynamic properties  
(conductivity, optical)

• Characterization —————> Understanding

## **FUEL CELLS:**

**Devices for Direct Conversion of Fuel to Electricity**

### **Advantages:**

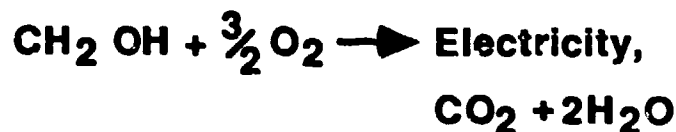
**High theoretical efficiency; low noise; low signature; no moving parts**

### **Problems:**

**Rate, density, fuel storage (H<sub>2</sub>)**

### **New Opportunity:**

**Low Temperature, Direct Use of Liquid Fuel**



### **Key Technical Hurdles:** CH<sub>3</sub>OH, O<sub>2</sub> Electrodes

**Require Improvement**

### **New Science:**

**Heterogeneous Catalysis**

**Underpotential Deposited Metals**

**Modified Electrodes**

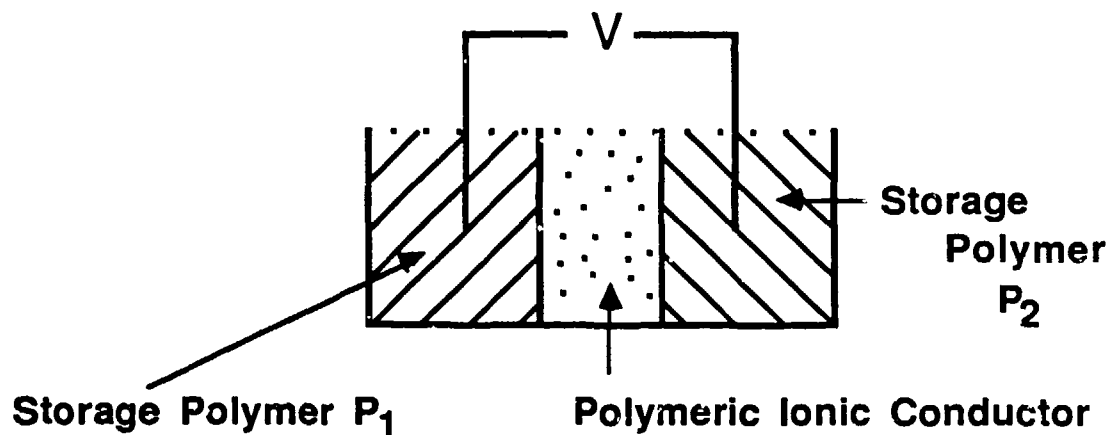
**Solid State Ionic Conductors**

## **POLYMER BATTERIES:** Rechargeable Power Sources

**Advantage:** Infinite number of 100% discharge/charge cycles

**Problems:** Rate, possibly density

**New Opportunity:** Integrated System



**Key Technical Hurdles:** Polymer/polymer interfaces  
Improve rate of discharge and fraction of atoms charged

**New Science:** Conducting Polymers  
Polymer/Polymer bilayers  
Ionic Conductors  
"Composite" Redox Polymers

# **MICROELECTROCHEMICAL DEVICES:**

## **Chemically Sensitive Analogues of Diodes and Transistors**

### **Advantages:**

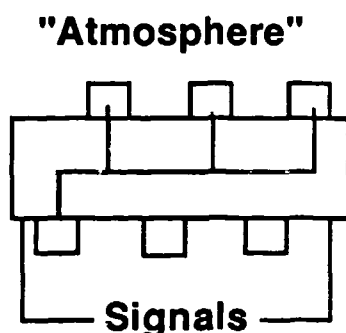
**Fast electrochemical devices, low power consumption, redundancy**

### **Problems:**

**To date, one-at-a-time "devices", Interface integrity, chemical specificity**

### **New Opportunity:**

**"Integrated" sensor array systems; microsensor array and microelectronics on a single chip**



### **Key Technical Hurdles:**

**Reproducible microfabrication for microelectrochemical devices, synthesis**

### **New Science:**

**Microelectrodes  
Microfabrication  
Redox Polymers, Synthesis  
Catalysis**

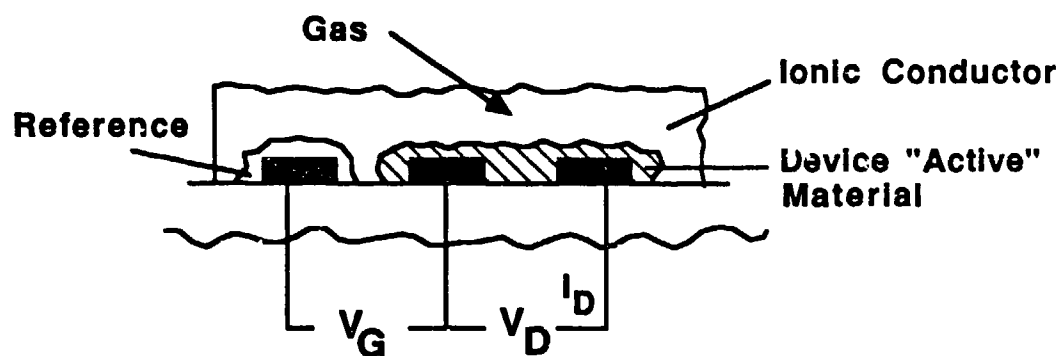
## **GAS DETECTORS:**

**Solid State Microelectrochemical Transistors**

**Advantages:** Small size, tailorability, speed

**Problems:** Specificity, dynamic range, calibration, stability

**New Opportunity:** Integration of new electrochemical and materials science



**Key Technical Hurdles:** Specificity of active material, prevent drift (better reference)

**New Service:**  
Heterogeneous Catalysis  
Microfabrication  
Conducting Polymers  
Ionic Conducting Polymers

## **ELECTROCHROMIC DISPLAYS:**

**Display systems based on color changes  
accompanying redox reaction**

**Advantages:** Full gray scale, viewable in bright light,  
bistable

**Problems:** Power consumption, speed, durability

**New Opportunity:** Use of new redox polymers

**Key Technical Hurdles:** Synthesis of redox polymers  
with  $\Delta\epsilon > 10^5$

**New Science:** Conducting Redox Polymers  
Chemical Synthesis  
Modified Electrodes

## **SUMMARY**

- **Exciting recent progress in chemical and materials science**
- **Proof-of-concept laboratory demonstrations of key "device" concepts**
- **"Integration" of science needed**
- **Cadre of "interdisciplinary" researchers**
- **DARPA Opportunities**
  - 1. New Power Sources**
  - 2. Tailored Microsensor Arrays**
  - 3. Materials Processing**
  - 4. Displays**

## MATERIALS SYNTHESIS IN ACADEMIC AND GOVERNMENT LABORATORIES

M. S. Wrighton

Materials synthesis is not a strong area in U.S. government laboratories at the present time. New compounds and materials reveal new physical phenomena and properties that can be exploited in practical applications. U.S. scientists have been strongly contributing to the discovery of new properties and phenomena including charge density waves, conducting polymers, high field superconductors, magnetic superconductors, intercalation compounds, and high dielectric constant microwave resonators. The troubling fact is that for each of the important discoveries mentioned above the prototype structure or compound was first reported by researchers in a foreign country. Many such synthesis efforts are associated with government laboratories or government-funded research. There is additional concern that non-U.S. discoveries of new materials properties and phenomena indicates that the U.S. is losing its edge. Developments having major technological significance. Foreign competitors realize the importance of new materials (and new methods for making materials) as an advantage in the search for new and superior materials properties.

The lack of a strong effort in materials synthesis in U.S. government laboratories parallels a weak effort in domestic universities. Curiously, though many of the leading research-oriented universities have strong efforts in molecular synthesis, the level of activity in materials synthesis is low in academic institutions. Even in the area of polymer materials, arguably the most important -- ?? -- of materials from molecular scientists, the U.S. academic institutions are weak performers. In our opinion, the number of innovative polymer synthesis programs in U.S. universities is less than ten.

Synthesis of inorganic solids is in no better shape. In the area of thin film microelectronics materials formed by CVD processes, it can be convincingly argued that much of the chemistry is being done by electrical engineers interested in the device characteristics of the materials being produced. While this situation is not intrinsically bad, the lack of innovative synthetic chemistry leads to use of "off-the-shelf" chemicals that can be acquired from commercial sources. New approaches to existing and new solid state materials and materials systems will require efforts that involve new synthesis. There are some signs of change in the academic scene, but there is much inertia in the academic system that will hinder rapid strengthening of materials synthesis programs in the academic sector.

Part of the difficulty in the present academic system is the fact that people who are creative in synthesis may not be aware of the needs and opportunities for new materials.

Further, the culture of chemistry has been such that a synthetic chemist could make new materials, albeit molecular materials, and fully characterize them within the confines of a small group of co-workers. As the data in Table 1 illustrate, the characterization of new solid materials must be extended well beyond the capabilities of a synthesis group. The recent advances in high  $T_c$  superconductors testifies amply to the fact that characterization of new materials must go far beyond establishment of composition and structure. There must develop an interaction between creative synthetic groups and others capable of complete characterization of materials properties.

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